



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification 6 : C01G 45/12, 45/02, H01M 4/50, B01J 23/32, A45D 20/40, A21B 2/00, H05B 3/10</p>	<p>A1</p>	<p>(11) International Publication Number: WO 00/27754 (43) International Publication Date: 18 May 2000 (18.05.00)</p>
<p>(21) International Application Number: PCT/US99/26343 (22) International Filing Date: 8 November 1999 (08.11.99) (30) Priority Data: 09/188,770 9 November 1998 (09.11.98) US 09/188,768 9 November 1998 (09.11.98) US 09/203,414 2 December 1998 (02.12.98) US 09/334,203 16 June 1999 (16.06.99) US (71) Applicant: NANOGRAM CORPORATION [US/US]; 46774 Lakeview Boulevard, Fremont, CA 94538 (US). (72) Inventors: KUMAR, Sujeet; 39800 Fremont Boulevard #206, Fremont, CA 94538 (US). BI, Xiangxin; 677 Graylyn Drive, San Ramon, CA 94583 (US). HORNE, Craig, R.; 3924 20th Street, San Francisco, CA 94110 (US). HARIKLIA, Dris, Reitz; 2147 Newhall Street #212, Santa Clara, CA 95050 (US). GARDNER, James, T.; 10251 Tantau Avenue, Cupertino, CA 95014 (US). MOSSO, Ronald, J.; 46553 Chaparral Drive, Fremont, CA 94539 (US). KAMBE, Nobuyuki; 840 Hobart Street, Menlo Park, CA 94025 (US).</p>		<p>(74) Agents: DARDI, Peter, S. et al.; Westman, Champlin &amp; Kelly, P.A., International Centre, Suite 1600, 900 Second Avenue South, Minneapolis, MN 55402-3319 (US). (81) Designated States: CA, CN, JP, KR, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  Published With international search report.</p>
<p>(54) Title: METAL OXIDE PARTICLES</p> <p>(57) Abstract</p> <p>Manganese oxide particles and lithium manganese oxide particles have been produced with an average diameter less than about 500 nm. The particles have a high degree of uniformity including a very narrow distribution of particles sizes. Methods are described for producing metal oxides by performing a reaction with an aerosol including a metal precursor. In particular, the particles can be formed by laser pyrolysis. The lithium manganese oxide particles can be formed by the heat treatment of nanoparticles of manganese oxide. Alternatively, lithium manganese oxide particles can be formed directly by laser pyrolysis. The lithium manganese oxide particles are useful as active materials in the positive electrodes of lithium based batteries. Improved batteries result from the use of the uniform nanoscale lithium manganese oxide particles.</p> <div data-bbox="678 1129 1399 1816"> </div>		

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## METAL OXIDE PARTICLES

### FIELD OF THE INVENTION

The invention relates to metal oxide powders. More particularly, the invention relates to nanoscale  
5 metal oxide particles, such as manganese oxide particles and lithium manganese oxide particles, produced by laser pyrolysis. The invention further relates to methods for producing metal oxide powders with laser pyrolysis and aerosol precursors. Furthermore, the invention relates  
10 to methods of producing ternary particles, especially crystalline nanoparticles, by laser pyrolysis.

### BACKGROUND OF THE INVENTION

Advances in a variety of fields have created a demand for many types of new materials. In  
15 particular, a variety of chemical powders can be used in many different processing contexts, such as the production of batteries. Specifically, there is considerable interest in the application of ultrafine or nanoscale powders that are particularly advantageous for  
20 a variety of applications involving small structures or high surface area materials. This demand for ultrafine chemical powders has resulted in the development of sophisticated techniques, such as laser pyrolysis, for the production of these powders.

25 The microminiaturization of electronic components has created widespread growth in the use of portable electronic devices such as cellular phones, pagers, video cameras, facsimile machines, portable stereophonic equipment, personal organizers and personal  
30 computers. The growing use of portable electronic equipment has created ever increasing demand for improved power sources for these devices. Relevant batteries include primary batteries, i.e., batteries

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designed for use through a single charging cycle, and secondary batteries, i.e., batteries designed to be rechargeable. Some batteries designed essentially as primary batteries may be rechargeable to some extent.

5           Batteries based on lithium have been the subject of considerable development effort and are being sold commercially. Lithium based batteries generally use electrolytes containing lithium ions. The negative electrodes for these batteries can include lithium metal  
10 or alloy (lithium batteries), or compositions that intercalate lithium (lithium ion batteries). Preferred electroactive materials for incorporation into the positive electrodes are compositions that intercalate lithium. The compositions that intercalate lithium, for  
15 use in the positive electrodes, generally are chalcogenides such as metal oxides that can incorporate the lithium ions into their lattice.

          Manganese can exist in various oxidation states. Correspondingly, manganese oxides are known to  
20 exist with various stoichiometries. In addition, manganese oxides with a particular stoichiometry can have various crystalline lattices, or they can be amorphous. Thus, manganese oxides exhibit an extraordinarily rich phase diagram.

25           Manganese oxides and lithium manganese oxides with various stoichiometries have been noted as promising materials for use in positive electrodes for lithium based batteries. In particular, appropriate manganese oxides can intercalate lithium ions into their  
30 crystal structure to form lithium manganese oxides. Lithium manganese oxides are useful for the production of lithium based secondary batteries. Because of the interest in lithium manganese oxides, several approaches



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have been developed for producing lithium manganese oxide powders.

#### SUMMARY OF THE INVENTION

In a first aspect, the invention pertains to  
5 a collection of particles comprising manganese oxide, the collection of particles having an average diameter less than about 500 nm, the manganese oxide having a structure selected from the group consisting of amorphous manganese oxide, crystalline MnO, crystalline  
10 Mn<sub>5</sub>O<sub>8</sub> and crystalline Mn<sub>2</sub>O<sub>3</sub>.

In another aspect, the invention pertains to a method of producing a metal oxide powder, the method comprising reacting an aerosol within a reaction chamber to form metal oxide particles, the aerosol comprising a  
15 metal precursor and the metal oxide particles having an average diameter less than about 500 nm.

In a further aspect, the invention pertains to a method for altering the stoichiometry of a collection of manganese oxide particles, the method comprising  
20 heating manganese oxide particles in an oxidizing environment at a temperature less than about 600°C.

In another aspect, the invention pertains to a battery having a cathode comprising manganese oxide particles, said manganese oxide particles having an  
25 average diameter less than about 250 nm.

In addition, the invention pertains to a method of producing a composite metal oxide particles, the method comprising reacting an aerosol to form a powder of composite metal oxide particles with an  
30 average diameter less than about one micron, the aerosol comprising a first metal compound precursor and a second metal compound precursor.

In a further aspect, the invention pertains to a method for producing lithium metal oxide, the method

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comprising pyrolyzing a reactant stream in a reaction chamber, the reactant stream comprising a lithium precursor, a non-lithium metal precursor, an oxidizing agent, and an infrared absorber, where the pyrolysis is  
5 driven by heat absorbed from a light beam.

In another aspect, the invention pertains to a collection of particles comprising lithium manganese oxide, the collection of particles having an average diameter less than about 250 nm, wherein the collection  
10 of particles have a distribution of particle sizes in which at least about 95 percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter.

Furthermore, the invention pertains to a method of making lithium manganese oxide particles comprising heating a mixture of manganese monoxide (MnO) particles and a lithium compound, the manganese monoxide  
15 particles having an average diameter less than about 250 nm.  
20 nm.

Moreover, the invention pertains to a method of making lithium manganese oxide particles comprising heating a mixture of particles of a manganese oxide and a lithium compound, the particles of manganese oxide  
25 having an average diameter less than about 250 nm, wherein the resulting lithium manganese oxide particles have a distribution of particle sizes in which at least about 95 percent of the particles have a diameter greater than about 40 percent of the average diameter  
30 and less than about 160 percent of the average diameter.

In a further aspect, the invention features a battery comprising lithium manganese oxide particles having an average diameter less than about 250 nm, wherein the lithium manganese oxide particles have a

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distribution of particle sizes in which at least about 95 percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter.

5           In another aspect, the invention features a battery comprising lithium manganese oxide, the battery having a four volt profile with a cycling stability within about 20 percent of initial values after 25 cycles.

10           In addition, the invention features a battery comprising lithium manganese oxide, the battery having an initial capacity greater than 120 mAh/g.

15           Moreover, the invention pertains to a collection of particles comprising lithium manganese oxide, the collection of particles having an average diameter less than about 250 nm, the lithium manganese oxide comprising  $\text{Li}_2\text{Mn}_4\text{O}_9$ .

20           In a further aspect, the invention pertains to a collection of particles comprising lithium manganese oxide, the collection of particles having an average diameter less than about 250 nm, the lithium manganese oxide having a lattice parameter along axis a of no more than 8.23 angstroms.

25           Furthermore, the invention pertains to a method of producing crystalline ternary particles comprising reacting a reactant stream comprising precursors including the three atoms of the product ternary particles, wherein the relative amounts of the  
30           three atoms in the reactant stream and the reaction conditions are selected to yield the crystalline ternary particles.

          In another aspect, the invention pertains to a method of producing crystalline lithium manganese

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oxide particles comprising reacting a reactant stream comprising a manganese precursor and a lithium precursor, wherein the reaction is driven by energy from electromagnetic radiation.

5 In a further aspect, the invention pertains to a collection of particles comprising a crystalline multiple metal oxide having an average particle diameter less than about 500 nm, wherein the lithium manganese oxide particles have a distribution of particle sizes in  
10 which at least about 95 percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter.

#### BRIEF DESCRIPTION OF THE DRAWINGS

15 Fig. 1 is a schematic sectional view of a solid precursor delivery system taken through the center of the system.

Fig. 2 is a schematic, sectional view of an embodiment of a laser pyrolysis apparatus, where the  
20 cross section is taken through the middle of the laser radiation path. The upper insert is a bottom view of the collection nozzle, and the lower insert is a top view of the injection nozzle.

Fig. 3 is a schematic, side view of a reactant  
25 delivery apparatus for the delivery of vapor reactants to the laser pyrolysis apparatus of Fig. 2.

Fig. 4A is a schematic, side view of a reactant delivery apparatus for the delivery of an aerosol reactant to the laser pyrolysis apparatus of  
30 Fig. 2.

Fig. 4B is a schematic, side view of an alternative embodiment of a reactant delivery apparatus for the delivery of an aerosol reactant to the laser pyrolysis apparatus of Fig. 2.

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Fig. 4C is a schematic, side view of another alternative embodiment of a reactant delivery apparatus for the delivery of an aerosol reactant to the laser pyrolysis apparatus of Fig. 2.

5 Fig. 5 is a schematic, perspective view of an elongated reaction chamber for the performance of laser pyrolysis, where components of the reaction chamber are shown as transparent to reveal internal structure.

10 Fig. 6 is a perspective view of an embodiment of an elongated reaction chamber for performing laser pyrolysis.

Fig. 7 is a cut away, side view of the reaction chamber of Fig. 6.

15 Fig. 8 is a partially sectional, front view of the reaction chamber of Fig. 6, taken along line 8-8 of Fig. 6.

20 Fig. 9 is a sectional, front view of a reactant delivery apparatus for the delivery of an aerosol reactant into the reaction chamber of Fig. 6, where the cross section is taken through the center of the reactant delivery apparatus.

Fig. 10 is a fragmentary, sectional front view of the top portion of the reactant delivery apparatus of Fig. 9.

25 Fig. 11 is a top view of the mount of the reactant delivery apparatus of Fig. 9.

Fig. 12 is a top view of a cap of the aerosol delivery apparatus of Fig. 9.

30 Fig. 13 is a sectional view of the cap of Fig. 12 taken along line 13-13.

Fig. 14 is a sectional side view of a spacer used in the aerosol delivery apparatus of Fig. 9, where the cross section is taken through the center of the spacer.

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Fig. 15 is a sectional side view of a shim used in the aerosol delivery apparatus of Fig. 9, where the cross section is taken through the center of the shim.

5            Fig. 16 is a sectional, side view of an embodiment of a brushing cap for use in the aerosol delivery apparatus of Fig. 9, where the cross section is taken through the center of the brushing cap.

10           Fig. 17 is a sectional, side view of an alternative embodiment of a brushing cap for use in the aerosol delivery apparatus of Fig. 9, where the cross section is taken through the center of the brushing cap.

15           Fig. 18 is a sectional, side view of a second alternative embodiment of a brushing cap for use in the aerosol delivery apparatus of Fig. 9, where the cross section is taken through the center of the brushing cap.

Fig. 19 is a side view of an ultrasonic aerosol generator having an atomization surface.

20           Fig. 20 is a sectional, side view of the ultrasonic aerosol generator of Fig. 19, where the cross section is taken through the center of the apparatus.

Fig. 21 is a schematic, side view of a liquid supply system for supplying liquid to the aerosol generator of Figs. 19 and 20.

25           Fig. 22A is a schematic, sectional view of an apparatus for heat treating nanoparticles, in which the section is taken through the center of the apparatus.

Fig. 22B is a schematic, sectional view of an oven for heating nanoparticles, in which the section is taken through the center of a quartz tube.

30           Fig. 23 is a schematic, perspective view of a battery of the invention.

Fig. 24 is an x-ray diffractogram of manganese oxide nanoparticles produced by laser pyrolysis with

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gaseous reactants according to the parameters specified in column 1 of Table 1.

Fig. 25 is an x-ray diffractogram of manganese oxide nanoparticles produced by laser pyrolysis with gaseous reactants according to the parameters specified in column 2 of Table 1.

Fig. 26 is an x-ray diffractogram of manganese oxide nanoparticles produced by laser pyrolysis with gaseous reactants according to the parameters specified in column 3 of Table 1.

Fig. 27 is a transmission electron micrograph of manganese oxide nanoparticles produced by laser pyrolysis with gaseous reactants according to the parameters specified in column 2 of Table 1.

Fig. 28 is a plot of particle diameter distribution for the particles shown in the transmission electron micrograph shown in Fig. 27.

Fig. 29 is an x-ray diffractogram of manganese oxide nanoparticles produced by laser pyrolysis with an aerosol manganese precursor according to the parameters specified in Table 2.

Fig. 30 is a transmission electron micrograph of manganese oxide nanoparticles produced by laser pyrolysis with an aerosol manganese precursor according to the parameters specified in Table 2.

Fig. 31 is a plot of particle size distribution for the particles shown in the transmission electron micrograph of Fig. 30.

Fig. 32 is an x-ray diffractogram of manganese oxide nanoparticles following a heat treatment of particles produced by laser pyrolysis, sample 1 of Table 3.

Fig. 33 is an x-ray diffractogram of manganese oxide nanoparticles following a heat treatment of

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particles produced by laser pyrolysis, sample 2A of Table 3.

Fig. 34 is an x-ray diffractogram of manganese oxide nanoparticles following a heat treatment of particles produced by laser pyrolysis, sample 2B of Table 3.

Fig. 35 is an x-ray diffractogram of manganese oxide nanoparticles produced by laser pyrolysis using with aerosol reactants according to the parameters specified in column 1 of Table 4.

Fig. 36 is an x-ray diffractogram of manganese oxide nanoparticles produced by laser pyrolysis using with aerosol reactants according to the parameters specified in column 2 of Table 4.

Fig. 37 is an x-ray diffractogram of nanoparticles of lithium manganese oxide produced by laser pyrolysis of a reactant stream with an aerosol.

Fig. 38 is an x-ray diffractogram of nanoparticles of lithium manganese oxide made by laser pyrolysis following heating in an oven.

Fig. 39 is a plot of three x-ray diffractograms for three samples of lithium manganese oxide produced by heat treating mixtures of nanocrystalline manganese oxide and lithium nitrate.

Fig. 40 is a transmission electron micrograph of manganese oxide nanoparticles used for further heating processing into lithium manganese oxide.

Fig. 41 is a transmission electron micrograph of lithium manganese oxide nanoparticles from sample 1.

Fig. 42 is an x-ray diffractogram for a sample of lithium manganese oxide particles directly produced by laser pyrolysis.



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Fig. 43 is a transmission electron micrograph of lithium manganese oxide particles corresponding to the x-ray diffractogram of Fig. 42.

5 Fig. 44 is a plot of two x-ray diffractograms of mixed phase materials including silver vanadium oxide nanoparticles produced directly by laser pyrolysis, where each plot is produced with materials produced under slightly different conditions.

10 Fig. 45A is a transmission electron micrograph of the materials from the sample corresponding to the upper diffractogram in Fig. 44.

Fig. 45B is a transmission electron micrograph of the materials from the sample corresponding to the lower diffractogram in Fig. 44.

15 Fig. 46 is a plot of particle size distribution for the particles shown in the transmission electron micrograph of Fig. 45.

Fig. 47 is a schematic, perspective view of the two electrode arrangement used in the examples.

20 Fig. 48 is a plot of cell voltage in a range of four volts for four different positive electrode active materials.

25 Fig. 49 is a plot of cell voltage in a range of three volts for four different positive electrode active materials.

Fig. 50 is a plot of capacity as a function of cycle number for eight different cells produced with four different positive electrode active materials.

30 Fig. 51 is a is a schematic, perspective view of the three electrode arrangement used for the following tests.

Fig. 52 is a plot of voltage as a function of specific capacity for two nanoscale samples and a commercial lithium manganese oxide.

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Fig. 53 is a plot of differential capacity for the samples used in Fig. 52.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

5               Several approaches are described for the production of metal oxide nanoparticles. These approaches provide for the production of metal oxide particles, such as manganese oxide nanoparticles, with a wide range of properties. Aerosol based approaches  
10 are described that can make use of low cost precursors to produce nanoparticles with a high production rate. Preferred collections of metal oxide particles have an average diameter less than a micron and a very narrow distribution of particle diameters. Laser pyrolysis  
15 with or without additional processing is a versatile approach for the production of a wide range of manganese oxide materials. The aerosol based approaches described herein can be used in the production of many other metal oxide nanoparticles.

20               In particular, several alternative approaches for the formation of nanoscale, crystalline ternary particles have been discovered. Crystalline, ternary particles has three types of atoms located at particular lattice sites within a crystal structure. Ternary  
25 particles of lithium metal oxide, such as lithium manganese oxide, are of particular interest because of their usefulness in battery applications.

              In a first approach, it has been discovered that nanoscale manganese oxides provide a suitable  
30 starting material for the formation of nanoscale lithium manganese oxides. In particular, lithium manganese oxides with an average diameter less than a micron can be formed with a spinel crystal structure by thermal processing approaches with nanoscale manganese oxide

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starting materials. The use of a nanoscale starting material allows for the use of very mild temperatures in the processing. The resulting nanoscale lithium manganese oxide spinels provide an excellent material for the formation of lithium based batteries.

Alternatively, lithium manganese oxide nanoparticles can be formed by laser pyrolysis. Amorphous lithium manganese oxide particles produced by laser pyrolysis can be heated under mild conditions to anneal the particles producing a spinel crystal structure. Furthermore, it has been discovered that crystalline lithium manganese oxide nanoparticles can be produced directly by laser pyrolysis. The lithium manganese oxide powders produced by laser pyrolysis can be subjected to a heat treatment to alter and/or improve the properties of the particles. Thus, alternative approaches have been found useful to produce lithium manganese oxide nanoparticles.

More specifically, in a first approach the lithium manganese oxide particles are formed by heating a mixture of nanoscale manganese oxide particles and a lithium compound. During the heating step the lithium is incorporated into the manganese oxide lattice. The manganese oxide particles for thermal lithium incorporation can have a variety of stoichiometries including, surprisingly,  $MnO$ . The heating can be performed either under an oxidizing atmosphere or under an inert atmosphere. Due to the nanoscale character of the manganese oxide starting material, the heating can be performed under surprisingly mild conditions. Under these mild reaction conditions, lithium manganese oxide particles are formed that have an average diameter less than a micron.

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A preferred approach for the formation of suitable nanoscale manganese oxide particles for lithiation involves laser pyrolysis. In particular, laser pyrolysis is an excellent process for efficiently  
5 producing manganese oxide particles and other metal oxide particles with a narrow distribution of average particle diameters.

A basic feature of successful application of laser pyrolysis for the production of metal oxide  
10 nanoparticles is the generation of a reactant stream containing a metal precursor compound, a radiation absorber and a secondary reactant. The secondary reactant can be an oxygen source. The reactant stream is pyrolyzed by an intense laser beam. As the reactant  
15 stream leaves the laser beam, the particles are rapidly quenched.

To perform laser pyrolysis, reactants can be supplied in vapor form. Alternatively, one or more reactants can be supplied as an aerosol. The use of an  
20 aerosol provides for the use of a wider range of metal precursors for laser pyrolysis than are suitable for vapor delivery only. Thus, less expensive precursors can be used with aerosol delivery. Suitable control of the reaction conditions with the aerosol results in  
25 nanoscale particles with a narrow particle size distribution. The heat processing of manganese oxide nanoparticles to form lithium manganese oxide nanocrystals and battery's formed from these nanoparticles are described below.

30 As an alternative to producing lithium manganese oxide nanoparticles by the thermal processing of manganese oxide particles, lithium manganese oxide particles having diameters substantially less than a micron have been produced directly by laser pyrolysis.

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For the direct production of lithium/manganese composite materials, laser pyrolysis preferably involves an aerosol based reactant delivery apparatus. Heat processing of the composite particles results in crystalline lithium manganese oxide particles with a spinel crystal structure. The formation of nanoscale, amorphous lithium manganese oxide directly by laser pyrolysis is described further below.

Laser pyrolysis experiments described below in the examples result in the production of amorphous lithium manganese oxide nanoparticles. In other experiments, the parameters of the laser pyrolysis synthesis have been adjusted to yield crystalline lithium manganese oxide nanoparticles directly by laser pyrolysis. These are also described below in the examples. The phase diagram of the materials to be produce can guide the selection of appropriate laser pyrolysis conditions. In addition, the parameters can be adjusted empirically to arrive at suitable conditions for the production of desired crystalline ternary particles. In particular, for the production of spinel  $\text{LiMn}_2\text{O}_4$ , production is favored by high chamber pressures, high flow rates of oxygen, low laser intensity for water based aerosols, and relatively higher laser intensity for aerosols based on water and isopropyl alcohol.

The production of a substituted metal oxide  $\text{Ti}_{1-x}\text{V}_x\text{O}_2$  by laser pyrolysis has been described by Musci et al., "Laser synthesis of vanadium-titanium oxide catalysts," J. Mater. Res. Vol. 7(10): 2846-2852 (October 1992), incorporated herein by reference. In these substituted metal oxides, vanadium substitutes at a lattice site for a titanium atom. The value of x could only be increased up to about 0.25 before a

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separate vanadium oxide phase formed. These substituted metal oxides are not crystalline ternary compounds since the metal atoms are not at unique lattice sites. In crystalline ternary compounds, each atom is located at a particular lattice site to yield a particular crystal structure. Similar substitution compounds with titanium substituting for chromium in  $\text{Cr}_2\text{O}_3$  were described by Schramm et al., U.S. Patent 5,013,706, "Metal Oxide Powders Or Their Mixtures And Their Use In Catalytic Dehydrogenation Of Hydrocarbons," incorporated herein by reference.

As noted above, various forms of manganese oxides and lithium manganese oxides can reversibly intercalate lithium atoms and/or ions. The manganese oxide and/or lithium manganese oxide nanoparticles can be incorporated into a positive electrode film with a binder such as a polymer. The film preferably includes additional electrically conductive particles held by the binder along with the lithium-manganese oxide particles. The positive electrode film can be used in a lithium battery or a lithium ion battery. The electrolyte for lithium and lithium ion batteries comprises lithium ions.

A. Particle Production Using Laser Pyrolysis

Laser pyrolysis has been discovered to be a valuable tool for the production of nanoscale metal oxide particles, in particular manganese oxide particles for further processing into lithium manganese oxide or for the direct production of lithium manganese oxide particles. In addition, the particles produced by laser pyrolysis are a convenient material for further processing to expand the pathways for the production of desirable metal oxide particles. Thus, using laser pyrolysis alone or in combination with additional

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processes, a wide variety of metal oxide particles can be produced.

Manganese oxide nanoparticles produced by laser pyrolysis are a preferred starting material for the lithium incorporation process described herein involving the mild heating of manganese oxide nanoparticles with a lithium compound. In addition, lithium manganese oxide nanoparticles can be produced directly by laser pyrolysis, where heating can be used to alter and/or improve the characteristics of the resulting particles. The lithium manganese oxide nanoparticles formed by laser pyrolysis can be either amorphous or crystalline.

The reaction conditions determine the qualities of the particles produced by laser pyrolysis. The reaction conditions for laser pyrolysis can be controlled relatively precisely in order to produce particles with desired properties. The appropriate reaction conditions to produce a certain type of particles generally depend on the design of the particular apparatus. Specific conditions used to produce manganese oxide particles in two particular apparatuses and lithium manganese oxide in the first particular apparatus with two different reactant delivery systems are described below in the Examples. Furthermore, some general observations on the relationship between reaction conditions and the resulting particles can be made.

Increasing the laser power results in increased reaction temperatures in the reaction region as well as a faster quenching rate. A rapid quenching rate tends to favor production of high energy phases, which may not be obtained with processes near thermal equilibrium. Similarly, increasing the chamber pressure

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also tends to favor the production of higher energy structures. Also, increasing the concentration of the reactant serving as the oxygen source in the reactant stream favors the production of particles with increased amounts of oxygen.

Reactant flow rate and velocity of the reactant gas stream are inversely related to particle size so that increasing the reactant gas flow rate or velocity tends to result in smaller particle sizes. Also, the growth dynamics of the particles have a significant influence on the size of the resulting particles. In other words, different forms of a product compound have a tendency to form different size particles from other phases under relatively similar conditions. Laser power also influences particle size with increased laser power favoring larger particle formation for lower melting materials and smaller particle formation for higher melting materials.

Laser pyrolysis has been performed generally with gas phase reactants. The use of exclusively gas phase reactants is somewhat limiting with respect to the types of precursor compounds that can be used. Thus, techniques have been developed to introduce aerosols containing reactant precursors into laser pyrolysis chambers. The aerosol atomizers can be broadly classified as ultrasonic atomizers, which use an ultrasonic transducer to form the aerosol, or as mechanical atomizers, which use energy from one or more flowing fluids (liquids, gases, or supercritical fluids) themselves to form the aerosol. Improved aerosol delivery apparatuses for reactant systems are described further in commonly assigned and copending U.S. Patent Application Serial Number 09/188,670 to Gardner et al.,



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entitled "Reactant Delivery Apparatuses," filed November 9, 1998, incorporated herein by reference.

Using aerosol delivery apparatuses, solid precursor compounds can be delivered by dissolving the compounds in a solvent. Alternatively, powdered precursor compounds can be dispersed in a liquid\solvent for aerosol delivery. Liquid precursor compounds can be delivered as an aerosol from a neat liquid, a multiple liquid dispersion or a liquid solution, if desired. Aerosol reactants can be used to obtain a significant reactant throughput. The solvent, if any, can be selected to achieve desired properties of the solution. Suitable solvents include water, methanol, ethanol, isopropyl alcohol, other organic solvents and mixtures thereof. The solvent should have a desired level of purity such that the resulting particles have a desired purity level. For the production of composite metal oxide particles by laser pyrolysis, a plurality of metal compounds can be included in the solution. Alternatively or additionally, metal precursors can be delivered into the reaction chamber in the vapor state in addition to the metal precursors delivered as an aerosol.

If aerosol precursors are formed with a solvent present, the solvent is rapidly evaporated by the laser beam in the reaction chamber such that a gas phase reaction can take place. Thus, the fundamental features of the laser pyrolysis reaction is unchanged. However, the reaction conditions are affected by the presence of the aerosol. Below, examples are described for the production of manganese oxide nanoparticles using gaseous reaction precursors and aerosol precursors using two different laser pyrolysis reaction chambers. The production of lithium manganese oxide nanoparticles

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by laser pyrolysis in one of these reaction chambers using aerosol precursors is also described in the Examples. Thus, the parameters associated with aerosol reactant delivery can be explored based on the description below.

A number of suitable solid, manganese precursor compounds can be delivered as an aerosol from solution. For example, manganese chloride ( $\text{MnCl}_2$ ) and hydrated manganese chloride ( $\text{MnCl}_2 \cdot \text{H}_2\text{O}$ ) are soluble in water and alcohols, and manganese nitrate ( $\text{Mn}(\text{NO}_3)_2$ ) is soluble in water and certain organic solvents. Also, suitable lithium precursors for aerosol delivery from solution include, for example, lithium chloride ( $\text{LiCl}$ ), which is somewhat soluble in water, alcohol and some other organic solvents, and lithium nitrate ( $\text{LiNO}_3$ ), which is somewhat soluble in water and alcohol. In addition, suitable vanadium precursors for aerosol delivery from solution include, for example,  $\text{VOCl}_2$ , which is soluble in absolute alcohol.

The compounds are dissolved in a solution preferably with a concentration greater than about 0.5 molar. Generally, the greater the concentration of precursor in the solution the greater the throughput of reactant through the reaction chamber. As the concentration increases, however, the solution can become more viscous such that the aerosol has droplets with larger sizes than desired. Thus, selection of solution concentration can involve a balance of factors in the selection of a preferred solution concentration.

For the formation of composite metal particles, the relative amounts of metal precursors in the solution effects the relative amounts of metals in the resulting particles. Thus, the desired composition of the product particles influences the selection of the

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relative amounts of metal precursors for delivery. While a desired stoichiometry may influence the relative amounts of metals delivered into the reaction chamber, the relative amounts of metal precursors may alter the portion of the phase diagram sampled such that a different material or mixed phase material can be produced. Since mixed phase materials may be produced, the relative amounts of metals in the reactant stream does not directly translate into particles with a corresponding stoichiometry.

As noted above, the reaction conditions determine the type and characteristics of the particles produced by laser pyrolysis. Of course, with the production of composite metal oxide particles, the situation is even more complicated because of the added complexity of the corresponding phase diagram. There is an additional parameter, namely, the quantity of additional metal precursor that effects the resulting properties of the particle(s). One can be guided by known stoichiometries of stable crystalline forms in the selection of the relative amounts of metal precursors, although phase diagrams may not be known completely, and the non-equilibrium conditions in the laser pyrolysis apparatus may lead to additional uncertainty.

In the production of lithium manganese oxide that the composition of the metal precursors influences the crystallinity of the resultant nanoparticles. In particular, metal chloride precursors favor the production of amorphous particles while metal nitrates favor the production of crystalline particles. Based on kinetic principles, higher quench rates favor amorphous particle formation while slower quench rates favor crystalline particle formation. Faster quenches are

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accomplished by a fasted reactant stream velocity through the reaction zone.

Appropriate manganese precursor compounds for gaseous delivery generally include manganese compounds with reasonable vapor pressures, i.e., vapor pressures sufficient to get desired amounts of precursor vapor in the reactant stream. The vessel holding liquid or solid precursor compounds can be heated to increase the vapor pressure of the manganese precursor, if desired. Suitable solid, manganese precursors with sufficient vapor pressure of gaseous delivery include, for example, manganese carbonyl ( $\text{Mn}_2(\text{CO})_{10}$ ). A suitable container for heating and delivering a solid precursor to a laser pyrolysis apparatus is shown in Fig. 1.

Referring to Fig. 1, the solid precursor delivery system 50 for vapor delivery includes a container 52 and a lid 54. A gasket 56 is located between container 52 and lid 54. In one preferred embodiment, container 52 and lid 54 are made from stainless steel, and gasket 56 is made from copper. In this embodiment, lid 54 and gasket 56 are bolted to container 52. Other inert materials, such as Pyrex®, suitable for the temperatures and pressures applied to the solid precursor system can be used. Container 52 is surrounded with a band heater 58, which is used to set the temperature of the delivery system 50 at desired values. Suitable band heaters are available from Omega Engineering Inc. Stamford, Conn. The temperature of the band heater can be adjusted to yield a desired vapor pressure of the precursor compound. Additional portions of the precursor delivery system can be heated to maintain the precursor in a vapor state after it has left container 52.

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Preferably, a thermocouple 60 is inserted into container 52 through lid 54. Thermocouple 60 can be inserted by way of a Swagelok® fitting 62 or other suitable connection. Tubing 64 provides a input flow of a carrier gas into container 52. Tubing 64 preferably includes a shut off valve 66 and can be inserted through lid 54 by way of a Swagelok® fitting 68 or other suitable connection. Output tube 70 also preferably includes a shut off valve 72. Output tube 70 preferably enters into container 52 through lid 54 at a sealed connection 74. Tubes 64 and 70 can be made of any suitable inert material such as stainless steel. A solid precursor can be placed directly within container 52 or it can be placed within a smaller, open container within container 52.

Preferred secondary reactants serving as oxygen source include, for example,  $O_2$ , CO,  $CO_2$ ,  $O_3$  and mixtures thereof. The secondary reactant compound should not react significantly with the manganese precursor and/or lithium precursor prior to entering the reaction zone since this generally would result in the formation of large particles.

Laser pyrolysis can be performed with a variety of optical frequencies. Preferred light sources operate in the infrared portion of the electromagnetic spectrum.  $CO_2$  lasers are particularly preferred sources of light. Infrared absorbers for inclusion in the molecular stream include, for example,  $C_2H_4$ ,  $NH_3$ ,  $SF_6$ ,  $SiH_4$  and  $O_3$ .  $O_3$  can act as both an infrared absorber and as an oxygen source. The radiation absorber, such as the infrared absorber, absorbs energy from the radiation beam and distributes the energy to the other reactants to drive the pyrolysis.

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Preferably, the energy absorbed from the light beam increases the temperature at a tremendous rate, many times the rate that heat generally would be produced even by strongly exothermic reactions under controlled condition. While the process generally involves nonequilibrium conditions, the temperature can be described approximately based on the energy in the absorbing region. The laser pyrolysis process is qualitatively different from the process in a combustion reactor where an energy source initiates a reaction, but the reaction is driven by energy given off by an exothermic reaction. Laser pyrolysis requires continuous input of laser energy to sustain the chemical reaction.

An inert shielding gas can be used to reduce the amount of reactant and product molecules contacting the reactant chamber components. Appropriate shielding gases include, for example, Ar, He and N<sub>2</sub>.

An appropriate laser pyrolysis apparatus generally includes a reaction chamber isolated from the ambient environment. A reactant inlet connected to a reactant supply system produces a reactant stream through the reaction chamber. A laser beam path intersects the reactant stream at a reaction zone. The reactant stream continues after the reaction zone to an outlet, where the reactant stream exits the reaction chamber and passes into a collection system. Generally, the laser is located external to the reaction chamber, and the light beam enters the reaction chamber through an appropriate window.

Two laser pyrolysis reaction chambers are described further below. These laser pyrolysis reaction chambers can be configured for delivery of gas phase reactants and/or aerosol reactants.

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1. First Laser Pyrolysis Reaction Chamber

Referring to Fig. 2, a particular embodiment 100 of a laser pyrolysis apparatus involves a reactant supply system 102, reaction chamber 104, collection system 106, laser 108 and shielding gas delivery system 110. Two alternative types of reaction supply systems can be used with the apparatus of Fig. 2. The first type of reaction supply system is used to deliver exclusively gaseous reactants. The second type of reactant supply system is used to deliver one or more reactants as an aerosol.

Referring to Fig. 3, a first embodiment 112 of reactant supply system 102 includes a source 120 of precursor compound. An optional second precursor source 121 can be used for the production of composite/ternary particles. For liquid or solid precursors, a carrier gas from one or more carrier gas sources 122 can be introduced into precursor source 120 and/or 121 to facilitate delivery of the precursor as a vapor. Precursor sources 120 and/or 121 can be a solid precursor delivery system 50, as shown in Fig. 1. The carrier gas from source 122 preferably is either an infrared absorber or an inert gas and is preferably bubbled through a liquid precursor compound or delivered into a solid precursor delivery system. Inert gas used as a carrier gas can moderate the reaction conditions. The quantity of precursor vapor in the reaction zone is roughly proportional to the flow rate of the carrier gas.

Alternatively, carrier gas can be supplied directly from infrared absorber source 124 or inert gas source 126, as appropriate. The secondary reactant can be supplied from reactant source 128, which can be a gas cylinder or other suitable container. The gases from

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the precursor sources 120, 121 are mixed with gases from reactant source 128, infrared absorber source 124 and inert gas source 126 by combining the gases in a single portion of tubing 130. The gases are combined a  
5 sufficient distance from reaction chamber 104 such that the gases become well mixed prior to their entrance into reaction chamber 104.

The combined gas in tube 130 passes through a duct 132 into rectangular channel 134, which forms part  
10 of an injection nozzle for directing reactants into the reaction chamber. Portions of reactant supply system 112 can be heated to inhibit the deposition of precursor compound on the walls of the delivery system.

Referring to Fig. 4A, a second embodiment 150  
15 of the reactant supply system 102 is used to supply an aerosol to duct 132. Duct 132 connects with rectangular channel 134, which forms part of an injection nozzle for directing reactants into the reaction chamber. Reactant supply system 150 includes a delivery tube 152 that is  
20 connected to duct 132. Venturi tube 154 connects to delivery tube 152 as a source of the aerosol. Venturi tube 154 is connected to gas supply tube 156 and liquid supply tube 158.

Gas supply tube 156 is connected to gas source  
25 160. Gas source 160 can include a plurality of gas containers that are connected to deliver a selected gas or gas mixture to gas supply tube 156. The flow of gas from gas source 160 to gas supply tube 156 is controlled by one or more valves 162. Liquid supply tube 158 is  
30 connected to liquid supply 164. Delivery tube 152 also connects with drain 166 that flows to reservoir 168.

In operation, gas flow through venturi tube 154 creates suction that draws liquid into venturi tube 154 from liquid supply tube 158. The gas-liquid mixture



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in venturi tube 154 forms an aerosol when venturi tube 154 opens into delivery tube 152. The aerosol is drawn up into duct 132 by pressure differentials within the system. Any aerosol that condenses within delivery tube 5 152 is collected in reservoir 168, which is part of the closed system.

Referring to Fig. 4B, a third embodiment 170 of the reactant supply system 102 can be used to supply an aerosol to duct 132. Reactant supply system 170 10 includes an aerosol generator 172, carrier gas/vapor supply tube 174 and junction 176. Duct 132, aerosol generator 172 and supply tube 174 meet within interior volume 178 of junction 176. Supply tube 174 is oriented to direct carrier gas along duct 132. Aerosol generator 15 172 is mounted such that an aerosol 180 is generated in the volume of chamber 178 between the opening into duct 132 and the outlet from supply tube 174.

Aerosol generator 172 can operate based on a variety of principles. For example, the aerosol can be 20 produced with an ultrasonic nozzle, with an electrostatic spray system, with a pressure-flow or simplex atomizer, with an effervescent atomizer or with a gas atomizer where liquid is forced under significant pressure through a small orifice and sheared into 25 droplets by a colliding gas stream. Suitable ultrasonic nozzles can include piezoelectric transducers. Ultrasonic nozzles with piezoelectric transducers and suitable broadband ultrasonic generators are available from Sono-Tek Corporation, Milton, NY, such as model 30 8700-120. Suitable aerosol generators are described further in copending and commonly assigned, U.S. Patent Application Serial No. 09/188,670 to Gardner et al., entitled "REACTANT DELIVERY APPARATUSES," incorporated herein by reference. Additional aerosol generators can

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be attached to junction 176 through other ports 182 such that additional aerosols can be generated in interior 178 for delivery into the reaction chamber.

Junction 176 includes ports 182 to provide  
5 access from outside junction 176 to interior 178. Thus, duct 132, aerosol generator 172 and supply tube 174 can be mounted appropriately. In one embodiment, junction 176 is cubic with six cylindrical ports 182, with one port 182 extending from each face of junction 176.  
10 Junction 176 can be made from stainless steel or other durable, noncorrosive material. A window 181 preferably is sealed at one port 182 to provide for visual observation into interior 178. The port 182 extending from the bottom of junction 176 preferably includes a  
15 drain 183, such that condensed aerosol that is not delivered through duct 132 can be removed from junction 176.

Carrier gas/vapor supply tube 174 is connected to gas source 184. Gas source 184 can include a  
20 plurality of gas containers, liquid reactant delivery apparatuses, and/or a solid reactant delivery apparatuses, which are connected to deliver a selected gas or gas mixture to supply tube 174. Thus, carrier gas/vapor supply tube 174 can be used to deliver a  
25 variety of desired gases and/or vapors within the reactant stream including, for example, laser absorbing gases, reactants, and/or inert gases. The flow of gas from gas source 184 to supply tube 174 preferably is controlled by one or more mass flow controllers 186.  
30 Liquid supply tube 188 is connected to aerosol generator 152. Liquid supply tube 188 is connected to liquid supply 189.

For the production of lithium manganese oxide particles, liquid supply 189 can hold a liquid

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comprising both a lithium precursor and a manganese precursor. Alternatively, for the production of lithium manganese oxide particles, liquid supply 189 can hold a liquid comprising manganese precursor while a lithium precursor is delivered by way of vapor supply tube 174 and gas source(s) 184. Similarly, if desired, liquid supply 189 can hold a liquid comprising lithium precursor, while a manganese precursor is delivered by way of vapor supply tube 174 and gas source(s) 184. Also, two separate aerosol generators 172 can be used to generate aerosol within junction 176, with one producing an aerosol with manganese precursor and the second producing aerosol with a lithium precursor.

In the embodiment shown in Fig. 4B, aerosol generator 172 generates an aerosol with momentum roughly orthogonal to the carrier gas flow from tube 174 to duct 132. Thus, carrier gas/vapor from supply tube 174 directs aerosol precursor generated by aerosol generator 172 into duct 132. In operation, carrier gas flow directs the aerosol delivered within chamber 178 into duct 132. In this way, the delivery velocity of the aerosol is determined effectively by the flow rate of the carrier gas.

In alternative preferred embodiments, the aerosol generator is placed at an upward angle relative to the horizontal, such that a component of the forward momentum of the aerosol is directed along duct 132. In a preferred embodiment, the output directed from the aerosol generator is placed at about a 45° angle relative to the normal direction defined by the opening into duct 132, i.e. the direction of the flow into duct 132 from supply tube 174.

Referring to Fig. 4C, another embodiment 191 of the reactant supply system 102 can be used to supply

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an aerosol to duct 132. Reactant supply system 191 includes an outer nozzle 193 and an inner nozzle 195. Outer nozzle 193 has an upper channel 197 that leads to a 5/8 in. by 1/4 in. rectangular outlet 199 at the top of outer nozzle 193, as shown in the insert in Fig. 4C. Outer nozzle 193 includes a drain tube 201 in base plate 203. Drain tube 201 is used to remove condensed aerosol from outer nozzle 193. Inner nozzle 195 is secured to outer nozzle 193 at fitting 205.

Inner nozzle 195 is a gas atomizer from Spraying Systems (Wheaton, IL), such as model number 17310-12-1x8jj. The inner nozzle has about a 0.5 inch diameter and a 12.0 inch length. The top of the nozzle is a twin orifice internal mix atomizer 207 (0.055 in. gas orifice and 0.005 in. liquid orifice). Liquid is fed to the atomizer through tube 209, and gases for introduction into the reaction chamber are fed to the atomizer through tube 211. Interaction of the gas with the liquid assists with droplet formation.

Outer nozzle 193 and inner nozzle 195 are assembled concentrically. Outer nozzle 193 shapes the aerosol generated by inner nozzle 195 such that it has a flat rectangular cross section. In addition, outer nozzle 193 helps to achieve a uniform aerosol velocity and a uniform aerosol distribution along the cross section. Outer nozzle 193 can be reconfigured for different reaction chambers. The height of outer nozzle 193 relative to the radiation/laser beam can be adjusted to produce spray characteristics that result in desired particle properties. For the production of lithium manganese oxide by laser pyrolysis, outer nozzle 193 is spaced about 3 inches below the laser beam.

Referring to Fig. 2, shielding gas delivery system 110 includes inert gas source 190 connected to an

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inert gas duct 192. Inert gas duct 192 flows into annular channel 194. A mass flow controller 196 regulates the flow of inert gas into inert gas duct 192. If reactant delivery system 112 is used, inert gas source 126 can also function as the inert gas source for duct 192, if desired.

The reaction chamber 104 includes a main chamber 200. Reactant supply system 102 connects to the main chamber 200 at injection nozzle 202. Reaction chamber 104 can be heated to keep the precursor compound in the vapor state. The chamber preferably is heated to a surface temperature above the dew point of the mixture of reactants and inert components at the pressure in the apparatus. For many embodiments, the chamber is heated to about 120° when a solid precursor is used. Similarly, for many embodiments, the argon shielding gas is preferably heated to about 150°C when a solid precursor is used. The chamber can be examined for condensation to ensure that precursor is not deposited on the chamber.

The end of injection nozzle 202 has an annular opening 204 for the passage of inert shielding gas, and a reactant inlet 206 for the passage of reactants to form a reactant stream in the reaction chamber. Reactant inlet 206 preferably is a slit, as shown in the lower insert of Fig. 2. Annular opening 204 has, for example, a diameter of about 1.5 inches and a width along the radial direction from about 1/8 in to about 1/16 in. The flow of shielding gas through annular opening 204 helps to prevent the spread of the reactant gases and product particles throughout reaction chamber 104.

Tubular sections 208, 210 are located on either side of injection nozzle 202. Tubular sections

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208, 210 include ZnSe windows 212, 214, respectively. Windows 212, 214 are about 1 inch in diameter. Windows 212, 214 are preferably cylindrical lenses with a focal length equal to the distance between the center of the chamber to the surface of the lens to focus the light beam to a point just below the center of the nozzle opening. Windows 212, 214 preferably have an antireflective coating. Appropriate ZnSe lenses are available from Laser Power Optics, San Diego, California. Tubular sections 208, 210 provide for the displacement of windows 212, 214 away from main chamber 200 such that windows 212, 214 are less likely to be contaminated by reactants and/or products. Window 212, 214 are displaced, for example, about 3 cm from the edge of the main chamber 200.

Windows 212, 214 are sealed with a rubber o-ring to tubular sections 208, 210 to prevent the flow of ambient air into reaction chamber 104. Tubular inlets 216, 218 provide for the flow of shielding gas into tubular sections 208, 210 to reduce the contamination of windows 212, 214. Tubular inlets 216, 218 are connected to inert gas source 190 or to a separate inert gas source. In either case, flow to inlets 216, 218 preferably is controlled by a mass flow controller 220.

Light source 108 is aligned to generate a light beam 222 that enters window 212 and exits window 214. Windows 212, 214 define a light path through main chamber 200 intersecting the flow of reactants at reaction zone 224. After exiting window 214, light beam 222 strikes power meter 226, which also acts as a beam dump. An appropriate power meter is available from Coherent Inc., Santa Clara, CA. Light source 108 can be a laser or an intense conventional light source such as an arc lamp. Preferably, light source 108 is an

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infrared laser, especially a CW CO<sub>2</sub> laser such as an 1800 watt maximum power output laser available from PRC Corp., Landing, NJ.

Reactants passing through reactant inlet 206 in injection nozzle 202 initiate a reactant stream. The reactant stream passes through reaction zone 224, where reaction involving the metal precursor compounds takes place. Heating of the gases in reaction zone 224 is extremely rapid, roughly on the order of 10<sup>5</sup> degree C/sec depending on the specific conditions. The reaction is rapidly quenched upon leaving reaction zone 224, and particles 228 are formed in the reactant stream. The nonequilibrium nature of the process allows for the production of nanoparticles with a highly uniform size distribution and structural homogeneity.

The path of the reactant stream continues to collection nozzle 230. Collection nozzle 230 is spaced about 2 cm from injection nozzle 202. The small spacing between injection nozzle 202 and collection nozzle 230 helps reduce the contamination of reaction chamber 104 with reactants and products. Collection nozzle 230 has a circular opening 232, as shown in the upper insert of Fig. 2. Circular opening 232 feeds into collection system 106.

The chamber pressure is monitored with a pressure gauge attached to the main chamber. The preferred chamber pressure for the production of the desired oxides generally ranges from about 80 Torr to about 650 Torr.

Reaction chamber 104 has two additional tubular sections not shown. One of the additional tubular sections projects into the plane of the sectional view in Fig. 2, and the second additional tubular section projects out of the plane of the

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sectional view in Fig. 2. When viewed from above, the four tubular sections are distributed roughly, symmetrically around the center of the chamber. These additional tubular sections have windows for observing the inside of the chamber. In this configuration of the apparatus, the two additional tubular sections are not used to facilitate production of particles.

Collection system 106 preferably includes a curved channel 270 leading from collection nozzle 230. Because of the small size of the particles, the product particles follow the flow of the gas around curves. Collection system 106 includes a filter 272 within the gas flow to collect the product particles. Due to curved section 270, the filter is not supported directly above the chamber. A variety of materials such as Teflon, glass fibers and the like can be used for the filter as long as the material is inert and has a fine enough mesh to trap the particles. Preferred materials for the filter include, for example, a glass fiber filter from ACE Glass Inc., Vineland, NJ and cylindrical Nomex® filters from AF Equipment Co., Sunnyvale, CA.

Pump 274 is used to maintain collection system 106 at a selected pressure. A variety of different pumps can be used. Appropriate pumps for use as pump 274 include, for example, Busch Model B0024 pump from Busch, Inc., Virginia Beach, VA with a pumping capacity of about 25 cubic feet per minute (cfm) and Leybold Model SV300 pump from Leybold Vacuum Products, Export, PA with a pumping capacity of about 195 cfm. It may be desirable to flow the exhaust of the pump through a scrubber 276 to remove any remaining reactive chemicals before venting into the atmosphere. The entire apparatus 100 can be placed in a fume hood for ventilation purposes and for safety considerations.



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Generally, the laser remains outside of the fume hood because of its large size.

The apparatus is controlled by a computer. Generally, the computer controls the light source and monitors the pressure in the reaction chamber. The computer can be used to control the flow of reactants and/or the shielding gas. The pumping rate is controlled by either a manual needle valve or an automatic throttle valve inserted between pump 274 and filter 272. As the chamber pressure increases due to the accumulation of particles on filter 272, the manual valve or the throttle valve can be adjusted to maintain the pumping rate and the corresponding chamber pressure.

The reaction can be continued until sufficient particles are collected on filter 272 such that pump 274 can no longer maintain the desired pressure in the reaction chamber 104 against the resistance through filter 272. When the pressure in reaction chamber 104 can no longer be maintained at the desired value, the reaction is stopped, and filter 272 is removed. With this embodiment, about 1-300 grams of particles can be collected in a single run before the chamber pressure can no longer be maintained. A single run generally can last up to about 10 hours depending on the reactant delivery system, the type of particle being produced and the type of filter being used.

The reaction conditions can be controlled relatively precisely. In particular, the mass flow controllers are quite accurate. The laser generally has about 0.5 percent power stability. With either a manual control or a throttle valve, the chamber pressure can be controlled to within about 1 percent.

The configuration of the reactant supply system 102 and the collection system 106 can be

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reversed. In this alternative configuration, the reactants are supplied from the top of the reaction chamber, and the product particles are collected from the bottom of the chamber. In the alternative configuration, the collection system may not include a curved section so that the collection filter is mounted directly below the reaction chamber.

2. Second Laser Pyrolysis Reaction Chamber

An alternative design of a laser pyrolysis apparatus has been described in U.S. Patent 5,958,348, entitled "Efficient Production of Particles by Chemical Reaction," incorporated herein by reference. This alternative design is intended to facilitate production of commercial quantities of particles by laser pyrolysis. The reaction chamber is elongated along the light beam in a dimension perpendicular to the reactant stream to provide for an increase in the throughput of reactants and products. The original design of the apparatus was based on the introduction of purely gaseous reactants. A particular embodiment for the introduction of an aerosol into the apparatus is described below. Additional embodiments for the introduction of an aerosol with one or more aerosol generators into an elongated reaction chamber is described in commonly assigned and copending U.S. Patent application serial No. 09/188,670 to Gardner et al., entitled "Reactant Delivery Apparatuses," filed November 9, 1998, incorporated herein by reference.

In general, the alternative pyrolysis apparatus includes a reaction chamber designed to reduce contamination of the chamber walls, to increase the production capacity and to make efficient use of resources. To accomplish these objectives, an elongated reaction chamber is used that provides for an increased

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throughput of reactants and products without a corresponding increase in the dead volume of the chamber. The dead volume of the chamber can become contaminated with unreacted compounds and/or reaction products.

The design of the improved reaction chamber 300 is shown schematically in Fig. 5. A reactant inlet 302 leads to main chamber 304. Reactant inlet 302 conforms generally to the shape of main chamber 304. The introduction of reactants through reactant inlet 302, for example, for the production of lithium manganese oxide particles can be performed by adapting the discussion above regarding the introduction of aerosol and/or vapor precursors with the laser pyrolysis apparatus of Fig. 1, appropriately adapted for the alternative structure of the reactant inlet. Generally, the reactant inlet has a length from about 5 mm to about 1 meter when used with an 1800 watt CO<sub>2</sub> laser.

Main chamber 304 includes an outlet 306 along the reactant/product stream for removal of particulate products, any unreacted gases and inert gases. Shielding gas inlets 310 are located on both sides of reactant inlet 302. Shielding gas inlets are used to form a blanket of inert gases on the sides of the reactant stream to inhibit contact between the chamber walls and the reactants or products.

Tubular sections 320, 322 extend from the main chamber 304. Tubular sections 320, 322 hold windows 324, 326 to define a light beam path 328 through the reaction chamber 300. Tubular sections 320, 322 can include inert gas inlets 330, 332 for the introduction of inert gas into tubular sections 320, 322.

Referring to Figs. 6-8, a specific embodiment 350 of a laser pyrolysis reaction system with an

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elongated reaction chamber is shown. In this embodiment, an aerosol reactant delivery apparatus is adapted for use with the elongated reaction chamber. Laser pyrolysis reaction system 350 includes reaction chamber 352, a particle collection system 354, laser 356 and a reactant delivery system (described below). Reaction chamber 352 includes reactant inlet 364 at the bottom of reaction chamber 352 where the reactant delivery system connects with reaction chamber 352. In this embodiment, the reactants are delivered from the bottom of the reaction chamber while the products are collected from the top of the reaction chamber. The configuration can be reversed with the reactants supplied from the top and product collected from the bottom, if desired.

Shielding gas conduits 365 are located on the front and back of reactant inlet 364. Inert gas is delivered to shielding gas conduits 365 through ports 367. The shielding gas conduits direct shielding gas along the walls of reaction chamber 352 to inhibit association of reactant gases or products with the walls.

Reaction chamber 352 is elongated along one dimension denoted in Fig. 6 by "w". A laser beam path 366 enters the reaction chamber through a window 368 displaced along a tube 370 from main chamber 372 and traverses the elongated direction of reaction chamber 352. The laser beam passes through tube 374 and exits window 376. In one preferred embodiment, tubes 370 and 374 displace windows 368 and 376 about 11 inches from main chamber 372. The laser beam terminates at beam dump 378. In operation, the laser beam intersects a reactant stream generated through reactant inlet 364.

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The top of main chamber 372 opens into particle collection system 354. Particle collection system 354 includes outlet duct 380 connected to the top of main chamber 372 to receive the flow from main chamber 372. Outlet duct 380 carries the product particles out of the plane of the reactant stream to a cylindrical filter 382. Filter 382 has a cap 384 on one end. The other end of filter 382 is fastened to disc 386. Vent 388 is secured to the center of disc 386 to provide access to the center of filter 382. Vent 388 is attached by way of ducts to a pump. Thus, product particles are trapped on filter 382 by the flow from the reaction chamber 352 to the pump. Suitable pumps were described above with respect to the first laser pyrolysis apparatus in Fig. 2. Suitable filters for use as filter 382 include, for example, an air cleaner filter for a Saab 9000 automobile (Purilator part A44-67), which is wax impregnated paper with Plasticol or polyurethane end cap 384.

Referring to Fig. 9, an aerosol delivery apparatus 480 includes an aerosol generator 482, which is supported by mount 484 and a cap 486. Aerosol delivery apparatus 480 is secured to reactant inlet 364 of reaction chamber 352 to extend within main chamber 372, shown in Figs. 6-8. Mount 484 is connected to a base plate 488. Base plate 488 is fastened to reactant inlet 364 with bolts 490. An o-ring or the like, suitably shaped, can be placed within hollow 492 to form a seal between base plate 488 and reactant inlet 364.

Referring to Figs. 10 and 11, mount 484 has a generally cylindrical shape. Mount 484 includes a lip 506 extending within cylindrical cavity 508. Lip 506 helps support aerosol generator 482. In this embodiment, lip 506 includes a notch 510, which allows

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a portion of aerosol generator 482 to extend past lip 506. Top surface 512 of mount 484 includes a hollow 514 for holding an o-ring or the like to form a seal with cap 486 or a spacer, described below. Mount 484 further  
5 includes threads 518 on the outer surface 520.

Referring to Figs. 10, 12 and 13, cap 486 attaches over the top of mount 484. Cap 486 includes threads 528 that are mated with threads 518 on mount 484. Flange 530 can be used to form a seal with an o-  
10 ring or the like. Surface 532 includes hollow 534. Hollow 534 can hold an o-ring or the like to form a seal with aerosol generator 482 or a shim, described further below.

Tube 536 is in fluid communication with cavity  
15 538. Tube 536 provides for gas flow into cavity 538. Cavity 538 vents through port 540. Tubes 542 provide for fluid flow through channels 544 into projecting tubes 546. In this embodiment, four projecting tubes 546 project toward the flow stream coming from aerosol  
20 generator 482 and port 540. Four projecting tubes 546 are symmetrically distributed around port 540. More or less than four projecting tubes 546 can be used, if desired. Gas can be supplied to tubes 536 and 542 through one or more ports 547 through base plate 488  
25 (Fig. 9) by way of stainless steel tubing or the like.

The use of projecting tubes 546 are particularly useful to mix reactants further within the reaction chamber away from aerosol generator 482. Using projecting tubes 546, gases such as reactant gases  
30 and/or radiation absorbing gases can be mixed within reaction chamber 352 with reactants from aerosol generator 482 and/or port 540. Laser beam path 548 intersects the reaction stream just above projecting tubes 546.

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The position of aerosol generator 482 relative to port 540 can affect the properties of the resulting reactant stream and thereby the properties of the reaction product. With an ultrasonic aerosol generator, the tip of the aerosol generator preferably is located between positions just slightly below the cap surface to just slightly above the cap surface.

Spacer 550, shown in Fig. 14, can be placed between cap 486 and mount 484 to change the position of aerosol generator 482 relative to port 540. Spacer 550 is a cylindrical piece with a hollow 552 along top surface 554 for holding an o-ring or the like. Top surface 554 seals against flange 530 of cap 486. Lower surface 556 of spacer 550 seals against top surface 512 of mount 484. A shim 558, as shown in Fig. 15, is correspondingly placed between cap 486 and aerosol generator 482. Top surface 560 of shim 558 engages the o-ring in hollow 534. Flange 562 engages the aerosol generator 482.

The flow of reactants into main chamber 372 can be affected by the placement of a cap bushing at the opening of port 540. More specifically, a cap bushing can help provide a more confined reactant stream within main chamber 372. Three embodiments of cap bushings 570, 572, 574 are shown in Figs. 16-18, respectively. Referring to Fig. 16, cap bushing 570 has a cylindrical passage 576 and a flat upper surface 578 generally perpendicular to the central axis of cylindrical passage 576. Referring to Fig. 17, cap bushing 572 has a conical passage 580 and a flat upper surface 582 generally perpendicular to the symmetry axis of conical passage 580. Referring to Fig. 18, cap bushing 574 has a conical passage 584 and a top surface with a flat section 586 and a conical section 588. Preferred

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embodiments of cap bushings have a sharp edge between the internal passage and the top surface.

Reaction chamber 352 and reactant supply system 480 preferably are constructed from stainless steel or other corrosion resistant metal. O-rings and other seals can be made from natural or synthetic rubber or other polymers.

Referring to Fig. 10, in a preferred embodiment, aerosol generator 482 includes an ultrasonic nozzle 600 and nozzle supply 602. Preferred ultrasonic nozzle 600 is a model 8700-120 from Sono-Tek Corporation, Milton, NY. Referring to Figs. 19-20, ultrasonic nozzle 600 includes a nozzle tip 604, a nozzle body 606, a connector 608 for connection to an ultrasonic generator, and a liquid connection 610 for connection to a liquid reservoir directly or by way of nozzle supply 602. The end of nozzle tip 604 is an atomization surface 612. The size and shape of atomization surface 612 can be varied to yield a desirable spacial distribution of aerosol particles.

Nozzle tip 604 is connected to nozzle body 606 at or near top surface 614. Ultrasonic transducer 616 is located within nozzle body 606 at a suitable position to vibrate nozzle tip 604. Generally, ultrasonic transducer 616 is located toward top surface 614. Preferred ultrasonic transducers include, for example, piezoelectric transducers. Preferably, ultrasonic transducer 616 includes two or more piezoelectric transducers 618 coupled to oscillate in phase such that the amplitudes of the two vibrating piezoelectric transducers add to create an additive force at atomizing surface 612.

Ultrasonic transducer 616 is connected to an ultrasonic generator by way of connector 608. The



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ultrasonic generator preferably is a broad band generator operating over a frequency range from about 20 kHz to about 120 kHz. The electrical signal from the ultrasonic generator is conveyed from connector 608 to  
5 ultrasonic transducer 616 by way of conductors 620.

Liquid flows from liquid connection 610 to atomization surface 612 through channel 622, which runs through nozzle body 606. Referring to Fig. 10, nozzle supply 602 is connected to liquid connection 610 with a  
10 liquid fitting 630. Nozzle supply 602 includes a needle valve with pneumatic control. Nozzle supply 602 has a pneumatic control inlet 632, a needle valve adjustment 634 and a liquid feedstock inlet 636. Pneumatic control inlet 632 and liquid feedstock inlet 636 are accessed  
15 through central channel 508, which extends through base plate 488.

Liquid feedstock inlet 636 is connected to a liquid supply apparatus 640, shown schematically in Fig. 21. Liquid supply apparatus 640 includes, at least, one  
20 liquid source 642, an outlet tube 644 and a gas supply tube 646. Tube 644 connects with fitting 648 to liquid feedstock inlet 636. Similarly, tube 644 is connected directly or indirectly to liquid source 642. Liquid source 642 also connects to gas supply tube 646. Gas  
25 supply tube connects to a gas source 666, which can be a gas cylinder or the like. Flow from gas source 666 to gas supply tube 646 is controlled by one or more valves 668. Gas under pressure from gas supply tube 646 forces liquid from liquid source 642 into tube 644.

30 Proper placement of liquid source 642 can result in gravity supplying the pressure as an alternative to using gas pressure. In other embodiments, mechanical pumps are used to supply a relatively constant amount of pressure within tube 644.

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Suitable pumps include, for example, centrifugal pumps and a plurality of syringe pumps that operate sequentially.

In use, the aerosol generator 482 produces an aerosol of a liquid supplied to aerosol generator 482. Aerosol generator 482 can deliver a gas along with the aerosol. Also, the aerosol can be combined with a gas supplied through tube 536. Thus, the aerosol and any gases supplied from aerosol generator 482 and/or tube 536 are directed into reaction chamber 352 near port 540 of cap 486. The aerosol and any gases emanating from aerosol generator 482 and/or tube 536 can be combined further within reaction chamber 352 with additional gases from projecting tubes 546. The resulting mixture of aerosol and gases is subsequently reacted within reaction chamber 352.

For the performance of laser pyrolysis based reaction synthesis, the aerosol/gas mixture generally includes one or more reactants in aerosol form, optionally, one or more additional reactant gases, a laser absorbing gas if the reactants and/or solvent(s) do not sufficiently absorb the laser radiation, and, optionally, an inert gas. The gases can be supplied from a pressurized cylinder or other suitable container. Multiple reactants can be mixed in the liquid phase and delivered as the aerosol.

Alternative aerosol generators can be used with the elongated reaction chamber. In addition, one or more aerosol generators can be configured with the elongated reaction chamber in a variety of ways.

B. Heat Processing

1. Particle Conditioning

As noted above, properties of the metal oxide particles can be modified by further processing.

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Suitable starting material for the heat treatment include metal oxide particles, such as, lithium manganese oxide particles, produced by laser pyrolysis. In addition, particles used as starting material can have been subjected to one or more prior heating steps under different conditions. For the heat processing of metal oxide particles formed by laser pyrolysis, the additional heat processing can improve the crystallinity, remove contaminants, such as elemental carbon, and possibly alter the stoichiometry, for example, by incorporation of additional oxygen or of atoms from other gaseous species. The use of sufficiently mild conditions, i.e., temperatures well below the melting point of the particles, results in the processing of the particles without significantly sintering the particles into larger particles.

The starting materials generally can be particles of any size and shape, although nanoscale particles are preferred starting materials. The nanoscale particles have an average diameter of less than about 1000 nm and preferably from about 5 nm to about 500 nm, and more preferably from about 5 nm to about 150 nm. Suitable nanoscale starting materials have been produced by laser pyrolysis.

The metal oxide particles are preferably heated in an oven or the like to provide generally uniform heating. The processing conditions generally are mild, such that significant amounts of particle sintering does not occur. The temperature of heating preferably is low relative to the melting point of both the starting material and the product material.

For certain target product particles, additional heating does not lead to further variation in the particle composition once equilibrium has been

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reached. The atmosphere for the heating process can be an oxidizing atmosphere or an inert atmosphere. In particular, for conversion of amorphous particles to crystalline particles or from one crystalline structure to a different crystalline structure of essentially the same stoichiometry, the atmosphere generally can be inert. The atmosphere over the particles can be static, or gases can be flowed through the system.

Appropriate oxidizing gases include, for example,  $O_2$ ,  $O_3$ ,  $CO$ ,  $CO_2$ , and combinations thereof. The  $O_2$  can be supplied as air. Oxidizing gases optionally can be mixed with inert gases such as  $Ar$ ,  $He$  and  $N_2$ . When inert gas is mixed with the oxidizing gas, the gas mixture can include from about 1 percent oxidizing gas to about 99 percent oxidizing gas, and more preferably from about 5 percent oxidizing gas to about 99 percent oxidizing gas. Alternatively, either essentially pure oxidizing gas or pure inert gas can be used, as desired.

The precise conditions can be altered to vary the type of metal oxide particles that are produced. For example, the temperature, time of heating, heating and cooling rates, the gases and the exposure conditions with respect to the gases can all be changed, as desired. Generally, while heating under an oxidizing atmosphere, the longer the heating period the more oxygen that is incorporated into the material, prior to reaching equilibrium. Once equilibrium conditions are reached, the overall conditions determine the crystalline phase of the powders.

A variety of ovens or the like can be used to perform the heating. An example of an apparatus 660 to perform this processing is displayed in Fig. 22A. Apparatus 660 includes a jar 662, which can be made from glass or other inert material, into which the particles

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are placed. Suitable glass reactor jars are available from Ace Glass (Vineland, NJ). The top of glass jar 662 is sealed to a glass cap 664, with a Teflon® gasket 666 between jar 662 and cap 664. Cap 664 can be held in place with one or more clamps. Cap 664 includes a plurality of ports 668, each with a Teflon® bushing. A multiblade stainless steel stirrer 670 preferably is inserted through a central port 668 in cap 664. Stirrer 670 is connected to a suitable motor.

One or more tubes 672 are inserted through ports 668 for the delivery of gases into jar 662. Tubes 672 can be made from stainless steel or other inert material. Diffusers 674 can be included at the tips of tubes 672 to disburse the gas within jar 662. A heater/furnace 676 generally is placed around jar 662. Suitable resistance heaters are available from Glas-col (Terre Haute, IN). One port preferably includes a T-connection 678. The temperature within jar 662 can be measured with a thermocouple 678 inserted through T-connection 678. T-connection 678 can be further connected to a vent 680. Vent 680 provides for the venting of gas circulated through jar 662. Preferably vent 680 is vented to a fume hood or alternative ventilation equipment.

Preferably, desired gases are flowed through jar 662. Tubes 672 generally are connected to an oxidizing gas source and/or an inert gas source. Oxidizing gas, inert gas or a combination thereof to produce the desired atmosphere are placed within jar 662 from the appropriate gas source(s). Various flow rates can be used. The flow rate preferably is between about 1 standard cubic centimeters per minute (sccm) to about 1000 sccm and more preferably from about 10 sccm to about 500 sccm. The flow rate generally is constant

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through the processing step, although the flow rate and the composition of the gas can be varied systematically over time during processing, if desired. Alternatively, a static gas atmosphere can be used.

5           For the processing of manganese oxide and lithium manganese oxide nanoparticles, for example, the temperatures preferably range from about 50°C to about 600°C and more preferably from about 50°C to about 550°C, and even more preferably from about 60°C to about 10   400°C. The heating preferably is continued for greater than about 5 minutes, and generally is continued for from about 2 hours to about 120 hours, preferably from about 2 hours to about 25 hours. Some empirical adjustment may be required to produce the conditions 15   appropriate for yielding a desired material. The use of mild conditions avoids interparticle sintering resulting in larger particle sizes. Some controlled sintering of the particles can be performed at somewhat higher temperatures to produce slightly larger, average 20   particle diameters.

          The conditions to convert crystalline  $\text{VO}_2$  to orthorhombic  $\text{V}_2\text{O}_5$  and 2-D crystalline  $\text{V}_2\text{O}_5$ , and amorphous  $\text{V}_2\text{O}_5$  to orthorhombic  $\text{V}_2\text{O}_5$  and 2-D crystalline  $\text{V}_2\text{O}_5$  are describe in copending and commonly assigned U.S. Patent 25   application serial number 08/897,903, to Bi et al., entitled "Processing of Vanadium Oxide Particles With Heat," incorporated herein by reference.

## 2. Thermal Production of Lithium Manganese Oxide

          In an alternative approach to the formation of 30   lithium manganese oxide nanoparticles, it has been discovered that heat processing can be used to form nanoscale lithium manganese oxides. In a preferred approach to the thermal formation of lithium manganese oxide, manganese oxide nanoscale particles first are

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mixed with a lithium compound. The resulting mixture is heated in an oven to form a lithium manganese oxide. The heating resulting in lithium incorporation into the manganese oxide lattice can be performed in an oxidizing environment or an inert environment. In either type of environment, the heating step generally results in alteration of the oxygen-to-manganese ratio, lithium-to-manganese ratio, lithium-to-oxygen ratio or a combination thereof.

The use of sufficiently mild conditions, i.e., temperatures well below the melting point of the manganese oxide particles, results in lithium incorporation into the manganese oxide particles without significantly sintering the particles into larger particles. The manganese oxide particles used for the lithiation process preferably are nanoscale manganese oxide particles. It has been discovered that spinel lithium manganese oxides can be formed from manganese oxides with an oxidation state less than +4. In particular, manganese oxides with an oxidation states from +2 ( $\text{MnO}$ ) to +4 ( $\text{MnO}_2$ ) can be used to form lithium manganese oxide spinels. Suitable manganese oxide nanoparticles can have a stoichiometry of, for example,  $\text{MnO}$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{Mn}_5\text{O}_8$ ,  $\text{MnO}_2$ , and corresponding mixed phase materials.

Suitable lithium compounds include for example, lithium nitrate ( $\text{LiNO}_3$ ), lithium chloride ( $\text{LiCl}$ ),  $\text{Li}_2\text{CO}_3$ ,  $\text{LiOH}$ ,  $\text{LiOH}\cdot\text{H}_2\text{O}$ ,  $\text{Li}_2\text{C}_2\text{O}_4$ ,  $\text{LiHC}_2\text{O}_4$ ,  $\text{LiHC}_2\text{O}_4\cdot\text{H}_2\text{O}$ ,  $\text{Li}_3\text{C}_6\text{H}_5\text{O}_7\cdot 4\text{H}_2\text{O}$ ,  $\text{LiCOOH}\cdot\text{H}_2\text{O}$ , and  $\text{LiC}_2\text{H}_3\text{O}_2\cdot\text{H}_2\text{O}$ . Lithium incorporation into manganese oxide nanoparticles with some of these lithium compounds may require oxygen in the atmosphere during the heat processing. Appropriate oxidizing gases include, for example,  $\text{O}_2$ ,  $\text{O}_3$ ,  $\text{CO}$ ,  $\text{CO}_2$  and combinations thereof. The reactant gas

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can be diluted with inert gases such as Ar, He and N<sub>2</sub>. For example, air and/or clean, dry air can be used as a source of oxygen and inert gas. Alternatively, the gas atmosphere can be exclusively inert gas. Lithium manganese oxides have been produced with either an inert atmosphere or an oxidizing atmosphere, as described in the Examples below.

In addition, the heat processing can result in an alteration of the crystal lattice and/or removal of adsorbed compounds on the particles to improve the quality of the particles. The processing generally of metal oxide nanoscale particles in an oven is discussed further in copending and commonly assigned, U.S. Patent Application Ser. No. 08/897,903, filed July 21, 1997, entitled "Processing of Vanadium Oxide Particles With Heat," incorporated herein by reference. In particular, heat processing under mild conditions can be used to alter the crystal structure of lithium manganese oxide nanoparticles formed by laser pyrolysis. Specifically, amorphous lithium manganese oxide can be annealed to crystalline, cubic spinel, lithium manganese oxide without sintering the particles into larger particles.

A variety of apparatuses can be used to perform the heat processing for lithium incorporation and/or annealing of a sample. For example, the heating apparatus shown in Fig. 22A, as described above, can be used to perform heat processing for lithium incorporation. Another embodiment of an apparatus 700 to perform this processing is displayed in Fig. 22B. Apparatus 700 includes a tube 702 into which the particles are placed. Tube 702 is connected to a reactant gas source 704 and inert gas source 706. Reactant gas, inert gas or a combination thereof are



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placed within tube 702 to produce the desired atmosphere.

Preferably, the desired gases are flowed through tube 702. Tube 702 is located within oven or furnace 708. Oven 708 maintains the relevant portions of the tube at a relatively constant temperature, although the temperature can be varied systematically through the processing step, if desired. Temperature in oven 708 generally is measured with a thermocouple 710. Vial 712 prevents loss of the particles due to gas flow. Vial 712 generally is oriented with the open end directed toward the direction of the source of the gas flow. To form lithium manganese oxide in the heating step, a mixture of manganese oxide particles and particles of lithium compound can be placed in tube 702 within a vial 712. In alternatively embodiments, lithium manganese oxide particles produced by laser pyrolysis are placed into vial 712 for heating in tube 702.

The precise conditions including type of oxidizing gas (if any), concentration of oxidizing gas, pressure or flow rate of gas, temperature and processing time can be selected to produce the desired type of product material. The temperatures generally are mild, i.e., significantly below the melting point of the material. The use of mild conditions avoids interparticle sintering resulting in larger particle sizes. Some controlled sintering of the particles can be performed in oven 708 at somewhat higher temperatures to produce slightly larger, average particle diameters.

For lithium incorporation into manganese oxide, the temperature preferably ranges from about 60°C to about 600°C and more preferably from about 100°C to about 550°C. The particles preferably are heated for

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about 5 minutes to about 300 hours. For the heat processing (annealing) of lithium manganese oxide produced by laser pyrolysis, the temperature preferably ranges from about 50°C to about 600°C and more preferably from about 50°C to about 550°C. The lithium manganese particles preferably are heated for about 5 minutes to about 100 hours. Some empirical adjustment may be required to produce the conditions appropriate for yielding a desired material.

10 C. Particle Properties

A collection of particles of interest, comprising, for example, either manganese oxides or lithium manganese oxides, generally has an average diameter for the primary particles of less than about 15 500 nm, preferably from about 5 nm to about 100 nm, more preferably from about 5 nm to about 50 nm. The primary particles usually have a roughly spherical gross appearance. Upon closer examination, crystalline particles generally have facets corresponding to the 20 underlying crystal lattice. Nevertheless, crystalline primary particles tend to exhibit growth that is roughly equal in the three physical dimensions to give a gross spherical appearance. In preferred embodiments, 95 percent of the primary particles, and preferably 99 25 percent, have ratios of the dimension along the major axis to the dimension along the minor axis less than about 2. Diameter measurements on particles with asymmetries are based on an average of length measurements along the principle axes of the particle.

30 Because of their small size, the primary particles tend to form loose agglomerates due to van der Waals and other electromagnetic forces between nearby particles. Nevertheless, the nanometer scale of the primary particles is clearly observable in transmission

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electron micrographs of the particles. The particles generally have a surface area corresponding to particles on a nanometer scale as observed in the micrographs. Furthermore, the particles can manifest unique properties due to their small size and large surface area per weight of material. For example, vanadium oxide nanoparticles generally exhibit surprisingly high energy densities in lithium batteries, as described in U.S. Patent 5,952,125, entitled "Batteries With Electroactive Nanoparticles," incorporated herein by reference.

The primary particles preferably have a high degree of uniformity in size. Laser pyrolysis, as described above, generally results in primary particles having a very narrow range of particle diameters. Furthermore, heat processing under mild conditions does not alter the very narrow range of particle diameters. With aerosol delivery, the distribution of particle diameters is particularly sensitive to the reaction conditions. Nevertheless, if the reaction conditions are properly controlled, a very narrow distribution of particle diameters can be obtained with an aerosol delivery system, as described above. As determined from examination of transmission electron micrographs, the primary particles generally have a distribution in sizes such that at least about 95 percent, and preferably 99 percent, of the primary particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter. Preferably, the primary particles have a distribution of diameters such that at least about 95 percent, and preferably 99 percent, of the primary particles have a diameter greater than about 60 percent of the average

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diameter and less than about 140 percent of the average diameter.

Furthermore, in preferred embodiments no primary particles have an average diameter greater than about 4 times the average diameter and preferably 3 times the average diameter, and more preferably 2 times the average diameter. In other words, the particle size distribution effectively does not have a tail indicative of a small number of particles with significantly larger sizes. This is a result of the small reaction region and corresponding rapid quench of the particles. An effective cut off in the tail of the size distribution indicates that there are less than about 1 particle in  $10^6$  have a diameter greater than a specified cut off value above the average diameter. Narrow size distributions, lack of a tail in the distributions and the roughly spherical morphology can be exploited in a variety of applications.

In addition, the nanoparticles generally have a very high purity level. The crystalline manganese oxide and lithium manganese oxide nanoparticles produced by the above described methods are expected to have a purity greater than the reactants because the crystal formation process tends to exclude contaminants from the lattice. Furthermore, crystalline manganese oxide particles produced by laser pyrolysis have a high degree of crystallinity. Similarly, the crystalline lithium manganese oxide nanoparticles produced by heat processing have a high degree of crystallinity. Impurities on the surface of the particles may be removed by heating the particles to achieve not only high crystalline purity but high purity overall.

Manganese oxides are known to exist in a wide range of oxidation states from +2 to +4. The most

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common stoichiometries for manganese oxides include  $\text{MnO}$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{Mn}_5\text{O}_8$ , and  $\text{MnO}_2$ .  $\text{MnO}$  and  $\text{Mn}_5\text{O}_8$  have only a single known crystalline phase. In particular,  $\text{MnO}$  has a cubic crystal structure while  $\text{Mn}_5\text{O}_8$  has a monoclinic crystal structure. Several of the manganese oxides can exist in alternative crystal structures. For example,  $\text{Mn}_3\text{O}_4$  has either a tetragonal or orthorhombic crystal structure.  $\text{Mn}_2\text{O}_3$  has either a cubic or a hexagonal crystal structure. Also,  $\text{MnO}_2$  has either a cubic, orthorhombic or tetragonal crystal structure.

Lithium manganese oxides have a complex phase diagram that reflects some of the complexity of the manganese oxide phase diagram. High lithium content spinel phases of lithium manganese oxide can have a stoichiometry over the range from  $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ , where  $0 \leq x \leq 0.33$ . In addition, oxygen rich (deficient,  $y$  negative) defect spinel phases exist with stoichiometries of  $\text{LiMn}_2\text{O}_{4+y}$ , where  $-0.4 \leq y \leq 0.5$ . Furthermore, the lithium manganese oxide can be lithium deficient corresponding to stoichiometries of  $\text{Li}_{1-z}\text{Mn}_2\text{O}_4$ ,  $0 \leq z \leq 0.2$ . Overall, the spinels and defect spinels cover stoichiometries of  $\text{Li}_{1+x-z}\text{Mn}_{2-x}\text{O}_{4+y}$ , where  $0 \leq x \leq 0.33$ ,  $-0.4 \leq y \leq 0.5$  and  $0 \leq z \leq 0.2$ . Other states of lithium manganese oxides are known, such as  $\text{Li}_2\text{MnO}_3$ ,  $\text{Li}_{0.33}\text{MnO}_2$ ,  $\text{Li}_4\text{Mn}_5\text{O}_{12}$ , tetragonal  $\text{Li}_x\text{Mn}_2\text{O}_4$ ,  $1.8 \leq x \leq 2.2$ ,  $\text{LiMnO}_2$ ,  $\text{Li}_2\text{MnO}_2$ , and  $\lambda\text{-MnO}_2$ .  $\lambda\text{-MnO}_2$  is formed by chemically extracting lithium from  $\text{LiMn}_2\text{O}_4$  with acid, e.g., 1M  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$ .  $\lambda\text{-MnO}_2$  has a structure of  $\text{Li}_x\text{Mn}_2\text{O}_4$ ,  $0.05 < x < 0.20$ , depending on the extraction conditions.

#### D. Battery Application of Lithium Manganese Oxides

Referring to Fig. 23, battery 750 has an negative electrode 752, a positive electrode 754 and separator 756 between negative electrode 752 and

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positive electrode 754. A single battery can include multiple positive electrodes and/or negative electrodes. Electrolyte can be supplied in a variety of ways as described further below. Battery 750 preferably includes current collectors 758, 760 associated with negative electrode 752 and positive electrode 754, respectively. Multiple current collectors can be associated with each electrode if desired.

Lithium has been used in reduction/oxidation reactions in batteries because it is the lightest metal and because it is the most electropositive metal. Certain forms of lithium manganese oxide are known to incorporate additional lithium ions into its structure through intercalation or similar mechanisms such as topochemical absorption. Intercalation of lithium ions into suitable forms of a lithiated lithium manganese oxide lattice forms  $\text{Li}_x\text{MnO}_y$ .

In lithium manganese oxide spinels, a portion of the lithium is at tetrahedral spinel lattice sites. Changes in lithium incorporation into the lattice can involve variations in the amount of lithium at the tetrahedral sites from about 0.1 to about 1.0 per two manganese atoms. At low enough lithium concentration, the spinel crystal structure collapses. Alternatively, additional lithium can occupy octahedral intercalation sites within the spinel lattice once the tetrahedral sites are essentially full.

Lithium intercalates into the lithium manganese oxide lattice during discharge of the battery. Upon discharge, the positive electrode acts as a cathode and the negative electrode acts as an anode. The lithium leaves the lattice upon recharging, i.e., when a voltage is applied to the cell such that electric current flows into the positive electrode due to the

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application of an external EMF to the battery. Appropriate lithium manganese oxides can be an effective electroactive material for a positive electrode in either a lithium or lithium ion battery.

5           There are several forms of lithium manganese oxide spinels suitable for use as a positive electrode active material within a lithium based battery. The stoichiometric spinel,  $\text{LiMn}_2\text{O}_4$ , is a normal spinel consisting of an oxygen close-packed lattice with  
10       lithium occupying one-eighth of the tetrahedral positions and manganese occupying one-half of the octahedral positions. If lithium is removed from this material within an electrochemical cell, the voltage of the cell is generally above 3.5V and typically above  
15       3.8V, and can extend to about 4.4V or higher. Such a voltage profile is referred to as a 4 volt profile and the capacity derived from the cell is referred to as a 4 volt capacity. A material possessing an appreciable amount of 4 volt capacity is referred to as a 4 volt  
20       material.

          If there is excess lithium, a lithium substituted spinel,  $\text{Li}_{1+y}\text{Mn}_{2-y}\text{O}_4$ , is formed where the excess lithium occupy the manganese sites. For values of y less than about 0.33, lithium can still be  
25       extracted, and a cell containing this material would exhibit a 4 volt profile. As y is increased, the amount of extractable lithium decreases with a concomitant decrease in the 4 volt capacity.

          For values around 0.33 with a stoichiometry of  
30        $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$  or  $\text{Li}_4\text{Mn}_5\text{O}_{12}$ , the material becomes a 3 volt material since only a minor amount of 4 volt capacity remains. Such a profile is referred to as a 3 volt profile and the capacity derived from the cell is referred to as a 3 volt capacity. A material possessing

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an appreciable amount of 3 volt capacity is referred to as a 3 volt material.

If there are cationic vacancies in the spinel, a defect spinel is formed with the general formula  $\text{Li}_{1-z}\text{Mn}_{2-2z}\text{O}_4$ . A common form is a defect spinel with  $z=0.11$  yielding  $\text{Li}_{0.89}\text{Mn}_{1.78}\text{O}_4$  or  $\text{Li}_2\text{Mn}_4\text{O}_9$ . This material is primarily a 3 volt material. Additionally, this material is a lower-temperature material that usually is synthesized in an oxygen-rich environment. Upon heating in an oxygen atmosphere to a high temperature or in an inert environment,  $\text{Li}_2\text{Mn}_4\text{O}_9$  converts into  $\text{LiMn}_2\text{O}_4$ .

Positive electrode 754 includes electroactive nanoparticles such as lithium manganese oxide nanoparticles held together with a binder such as a polymeric binder. Nanoparticles for use in positive electrode 754 generally can have any shape, e.g., roughly spherical nanoparticles or elongated nanoparticles. In addition to lithium manganese oxide, positive electrode 754 can include other electroactive nanoparticles such as  $\text{TiO}_2$  nanoparticles, vanadium oxide nanoparticles, and/or manganese oxide nanoparticles. The production of  $\text{TiO}_2$  nanoparticles has been described, see U.S. Patent Ser. No. 4,705,762, incorporated herein by reference. The use of vanadium oxide nanoparticles in lithium based batteries is described in U.S. Patent 5,952,125, entitled "Batteries With Electroactive Nanoparticles," incorporated herein by reference.

While some electroactive materials are reasonable electrical conductors, a positive electrode generally includes electrically conductive particles in addition to the electroactive nanoparticles. These supplementary, electrically conductive particles generally are also held by the binder. Suitable electrically conductive particles include conductive



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carbon particles such as carbon black, metal particles such as silver particles, stainless steel fibers and the like.

High loadings of particles can be achieved in the binder. Particles preferably make up greater than about 80 percent by weight of the positive electrode, and more preferably greater than about 90 percent by weight. The binder can be any of various suitable polymers such as polyvinylidene fluoride, polyethylene oxide, polyethylene, polypropylene, polytetrafluoroethylene, polyacrylates, ethylene-(propylene-diene monomer) copolymer (EPDM) and mixtures and copolymers thereof.

Negative electrode 752 can be constructed from a variety of materials that are suitable for use with lithium ion electrolytes. In the case of lithium batteries, the negative electrode can include lithium metal or lithium alloy metal either in the form of a foil, grid or metal particles in a binder.

Lithium ion batteries use particles of an composition that can intercalate lithium. The particles are held with a binder in the negative electrode. Suitable intercalation compounds include, for example, graphite, synthetic graphite, coke, mesocarbons, doped carbons, fullerenes, niobium pentoxide, tin alloys,  $\text{SnO}_2$ , and mixtures and composites thereof.

Current collectors 758, 760 facilitate flow of electricity from battery 750. Current collectors 758, 760 are electrically conductive and generally made of metal such as nickel, iron, stainless steel, aluminum and copper and can be metal foil or preferably a metal grid. Current collector 758, 760 can be on the surface of their associated electrode or embedded within their associated electrode.

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The separator element 756 is electrically insulating and provides for passage of at least some types of ions. Ionic transmission through the separator provides for electrical neutrality in the different sections of the cell. The separator generally prevents electroactive compounds in the positive electrode from contacting electroactive compounds in the negative electrode.

A variety of materials can be used for the separator. For example, the separator can be formed from glass fibers that form a porous matrix. Preferred separators are formed from polymers such as those suitable for use as binders. Polymer separators can be porous to provide for ionic conduction. Alternatively, polymer separators can be solid electrolytes formed from polymers such as polyethylene oxide. Solid electrolytes incorporate electrolyte into the polymer matrix to provide for ionic conduction without the need for liquid solvent.

Electrolytes for lithium batteries or lithium ion batteries can include any of a variety of lithium salts. Preferred lithium salts have inert anions and are nontoxic. Suitable lithium salts include, for example, lithium hexafluorophosphate, lithium hexafluoroarsenate, lithiumbis(trifluoromethylsulfonyl imide), lithium trifluoromethane sulfonate, lithium tris(trifluoromethyl sulfonyl) methide, lithium tetrafluoroborate, lithium perchlorate, lithium tetrachloroaluminate, lithium chloride and lithium perfluorobutane.

If a liquid solvent is used to dissolve the electrolyte, the solvent preferably is inert and does not dissolve the electroactive materials. Generally appropriate solvents include, for example, propylene

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carbonate, dimethyl carbonate, diethyl carbonate, 2-methyl tetrahydrofuran, dioxolane, tetrahydrofuran, 1, 2-dimethoxyethane, ethylene carbonate,  $\gamma$ -butyrolactone, dimethyl sulfoxide, acetonitrile, formamide, dimethylformamide and nitromethane.

The shape of the battery components can be adjusted to be suitable for the desired final product, for example, a coin battery, a rectangular construction or a cylindrical battery. The battery generally includes a casing with appropriate portions in electrical contact with current collectors and/or electrodes of the battery. If a liquid electrolyte is used, the casing should prevent the leakage of the electrolyte. The casing can help to maintain the battery elements in close proximity to each other to reduce resistance within the battery. A plurality of battery cells can be placed in a single case with the cells connected either in series or in parallel.

## PARTICLE SYNTHESIS EXAMPLES

### Example 1 - Manganese Oxide Particle Synthesis, Gas Phase Reactants

The synthesis of manganese oxide particles described in this example was performed by laser pyrolysis. The particles were produced using essentially the laser pyrolysis apparatus of Fig. 2, described above, using the reactant delivery apparatus of Fig. 3 along with the solid precursor delivery system shown schematically in Fig. 1.

The manganese carbonyl (Strem Chemical, Inc., Newburyport, MA) precursor vapor was carried into the reaction chamber by flowing Ar gas through the solid precursor delivery system containing the  $\text{Mn}_2(\text{CO})_{10}$ . The precursor was heated to a temperature as indicated in

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Table 1.  $C_2H_4$  gas was used as a laser absorbing gas, and Argon was used as an inert gas. The reaction gas mixture containing  $Mn_2(CO)_{10}$ , Ar,  $O_2$  and  $C_2H_4$  was introduced into the reactant gas nozzle for injection into the reaction chamber. The reactant gas nozzle had an opening with dimensions of 5/8 in. x 1/16 in. Additional parameters of the laser pyrolysis synthesis relating to the particles of Example 1 are specified in Table 1.

TABLE 1

	1	2	3
Crystalline Phase	Manganosite	Manganosite	Manganosite & unidentified
Crystal Structure	Cubic	Cubic	Cubic
Pressure (Torr)	180	320	430
Argon F.R.- Window (SCCM)	700	700	700
Argon F.R.- Shielding (SLM)	1.71	1.99	1.99
Ethylene (SCCM)	492	517	517
Carrier Gas (Argon) SCCM	507	507	627
Oxygen (SCCM)	348	400	420
Laser Output (Watts)	260	108	206
Precursor Temperature °C	140	140	150

sccm = standard cubic centimeters per minute  
 slm = standard liters per minute  
 Argon - Win. = argon flow through inlets 216, 218  
 Argon - Sld. = argon flow through annular channel 142.

The production rate of manganese oxide particles was typically about 1 g/hr. To evaluate the atomic arrangement, the samples were examined by x-ray diffraction using the  $Cu(K\alpha)$  radiation line on a Siemens D500 x-ray diffractometer. X-ray diffractograms for a

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sample produced under the conditions specified in the three columns of Table 1 is shown in Figs. 24-26, respectively. Under the set of conditions specified in Table 1, the particles had an x-ray diffractogram  
5 corresponding to manganosite (cubic) MnO. The particles produced under the conditions in the third column of Table 1 also had a peak at 65° produced by the aluminum samples holder. The sample holder is occasionally seen in the diffractogram. The diffractograms may also have  
10 peaks indicating the presence of small amounts of amorphous carbon, which can form as a coating on the particles. The amorphous carbon can be removed by gentle heating in an oxygen environment. Such coating of amorphous carbon are described further in copending  
15 and commonly assigned U.S. Patent Application serial number 09/136,483 to Kumar et al., entitled "Aluminum Oxide Particles," incorporated herein by reference.

Transmission electron microscopy (TEM) was used to determine particle sizes and morphology. A TEM  
20 photograph of the particles produced under the conditions in the second column of Table 1 are shown in Fig. 27. An examination of a portion of the TEM micrograph yielded an average particle size of about 9 nm. The corresponding particle size distribution is  
25 shown in Fig. 28. The approximate size distribution was determined by manually measuring diameters of the particles distinctly visible in the micrograph of Fig. 27. Only those particles having clear particle boundaries were measured to avoid regions distorted or  
30 out of focus in the micrograph. Measurements so obtained should be more accurate and are not biased since a single view cannot show a clear view of all particles. It is significant that the particles span a rather narrow range of sizes.

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Example 2 - Manganese Oxide Particle Synthesis - Aerosol  
Metal Precursors, First Laser Pyrolysis Apparatus

The synthesis of manganese oxide particles described in this example was performed by laser  
5 pyrolysis. The particles were produced using essentially the laser pyrolysis apparatus of Fig. 2, described above, using the reactant delivery apparatus of Fig. 4A.

The manganese chloride (Alfa Aesar, Inc., Ward  
10 Hill, MA) precursor vapor was carried into the reaction chamber as an aerosol of an aqueous solution formed with deionized water.  $C_2H_4$  gas was used as a laser absorbing gas, and Argon was used as an inert gas. The reactant mixture containing  $MnCl_2$ , Ar,  $O_2$  and  $C_2H_4$  was introduced  
15 into the reactant nozzle for injection into the reaction chamber. The reactant nozzle had an opening with dimensions of 5/8 in. x 1/16 in. Additional parameters of the laser pyrolysis synthesis relating to the particles of Example 2 are specified in Table 2.

TABLE 2

20

	1
Crystalline Phase	Amorphous + Manganosite (MnO)
Crystal Structure	Amorphous + Cubic
Pressure (Torr)	350
25 Argon F.R.-Window (SCCM)	700
Argon F.R.-Shielding (SLM)	6.8
Ethylene (SLM)	1.27
Carrier Gas (Argon) SLM	6.35
Oxygen (SCCM)	883
30 Laser Output (Watts)	660
Precursor	Manganese Chloride solution in water
Precursor Molarity	2 M

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Precursor Temperature °C	Room Temperature
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sccm = standard cubic centimeters per minute

slm = standard liters per minute

5 Argon - Win. = argon flow through inlets 216, 218

Argon - Sld. = argon flow through annular channel 142.

The production rate of manganese oxide particles was typically about 1 g/hr. To evaluate the atomic arrangement, the samples were examined by x-ray diffraction using the Cu(K $\alpha$ ) radiation line on a Siemens D500 x-ray diffractometer. X-ray diffractograms for a sample produced under the conditions specified in Table 2 is shown in Fig. 29. The particles again had an x-ray diffraction pattern corresponding to manganosite (cubic) MnO, although the peaks in the x-ray diffractogram were very weak indicating that the particles were substantially amorphous. Based on these results, variations in the reaction conditions should result in either amorphous MnO or more highly crystalline MnO.

Transmission electron microscopy (TEM) was used to determine particle sizes and morphology. A TEM micrograph for the particles produced under the conditions of Table 2 is displayed in Fig. 30. The corresponding particle size distribution is shown in Fig. 31. The particle size distribution was obtained following the procedure described in Example 1.

#### Example 3 - Manganese Oxide Particles Heat Treated Samples

30 Samples of manganese oxide nanoparticles produced by laser pyrolysis according to the conditions specified in the second column of Table 1 and in Table 2 were heated in an oven under oxidizing conditions. Three samples were heat treated. Two separate samples were heat processed starting with the nanoparticles

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produced under the conditions in Table 2. The oven was essentially as described above with respect to Fig. 5. Between about 100 and about 300 mg of nanoparticles were placed in an open 1 cc vial within the quartz tube projecting through the oven. Oxygen gas was flowed through a 1.0 in diameter quartz tube. Other parameters of the heat processing are specified in Table 3.

Table 3

	Temperature	Time	Oxygen Flow Rate	Crystalline Phase
Sample 1	480 °C	3 hrs	200 cc/min	Mn <sub>5</sub> O <sub>8</sub>
Sample 2A	480	5 hrs	300 cc/min	Mn <sub>3</sub> O <sub>4</sub> , Mn <sub>2</sub> O <sub>3</sub>
Sample 2B	300	20 hrs	350 cc/min	Mn <sub>3</sub> O <sub>4</sub>

Sample 1 - Sample prepared from particles produced according to the parameters in the second column of Table 1.

Samples 2A & 2B - Samples prepared from particles produced according to the parameters of Table 2.

The crystal structure of the resulting heat treated particles were determined by x-ray diffraction. The x-ray diffractogram for samples 1, 2A and 2B of Table 3 are shown in Figs. 32-34, respectively. The x-ray diffractogram shown in Fig. 32 indicates that the manganese oxide in Sample 1 was converted to a form with a stoichiometry of Mn<sub>5</sub>O<sub>8</sub>. The x-ray diffractogram of Sample 2A shown in Fig. 33 indicates the presence of Mn<sub>3</sub>O<sub>4</sub>, with additional peaks in the spectrum at 23° and 33° corresponding to a minor amount of Mn<sub>2</sub>O<sub>3</sub>. The x-ray diffractogram of Sample 2B in Fig. 34 indicates that the manganese oxide was converted to Mn<sub>3</sub>O<sub>4</sub>. It is not clear why the MnO samples upon heat treatment resulted in different stoichiometries of manganese oxide. The different results may be due to the different properties



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of the starting materials or the different amounts of heating times.

Example 4 - Manganese Oxide Particle Synthesis - Aerosol Metal Precursors, Second Laser Pyrolysis Apparatus

5           The synthesis of manganese oxide particles described in this example was performed by laser pyrolysis. The particles were produced using a laser pyrolysis apparatus essentially as shown in Figs. 6-13, described above and the ultrasonic nozzle essentially as  
10 shown in Figs. 19-20. No cap bushing was used. A spacer 550 and shim 558 was used to raise the level of the ultrasonic nozzle to approximately the top of the cap. The solution delivered by the aerosol delivery apparatus contained 2 molar  $\text{MnNO}_3 \cdot \text{H}_2\text{O}$  (Strem Chemical,  
15 Inc., Newburyport, MA) in solvent formed from 495ml of 99% isopropyl alcohol and 5ml of 38% aqueous HCl. Isopropyl alcohol acts as a infrared absorber. Oxygen was mixed with the aerosol by delivery through tube 536. Projecting tubes 546 in Fig. 10 were not present. The  
20 top of cap 486 was about 0.85 inches from the center line of the laser beam. Additional parameters for two runs are presented in Table 4.

Table 4

	1	2
25 Crystalline Phase	$\text{MnO} + \text{Mn}_3\text{O}_4$	$\text{MnO} + \text{Mn}_3\text{O}_4$
Pressure (Torr)	300	200
Argon Window (SLM)	25	7.5
Argon Shielding (SLM)	40	70
Oxygen (SLM)	5	5
30 Laser Power (input) (watts)	1500	1800

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5	Laser Power (output) (watts)	1300	1300
	Absorbed Laser Power (Watts)	200	500
	Mass of Powder Recovered	3.4	5.0
	Run Duration (min.)	about 30	<30
	Ultrasonic Transducer Power (Watts)	2.3	4.6

10 sccm = standard cubic centimeters per minute  
 slm = standard liters per minute  
 Argon - Win. = argon flow through inlets 330, 332  
 Argon - Sld. = argon flow through shielding gas conduits  
 15 365.  
 Laser Power (input) = Laser power input into reaction  
 chamber.  
 Laser Power (output) = Laser power exiting the reaction  
 chamber into the beam dump.

20 Powder manganese oxide was made at a rate of  
 roughly 20 g/hr. The conditions specified in column 1  
 of Table 4 resulted in brown powder while the parameters  
 specified in the second column of Table 4 resulted in  
 25 yellow powder.

To evaluate the atomic arrangement, the  
 samples were examined by x-ray diffraction using the  
 Cu(K $\alpha$ ) radiation line on a Siemens D500 x-ray  
 diffractometer. X-ray diffractograms for a sample  
 30 produced under the conditions specified in column 1 and  
 column 2 of Table 4 is shown in Figs. 35 and 36,  
 respectively. The particles produced under the  
 conditions in columns 1 and 2 of Table 4 had x-ray  
 diffractograms indicating the presence of both  
 35 manganosite (cubic) MnO and hausmannite Mn<sub>3</sub>O<sub>4</sub>.

Example 5 - Lithium Manganese Oxide Particles by Laser  
 Pyrolysis - Aerosol Metal Precursors

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The synthesis of manganese oxide/lithium manganese oxide particles described in this example was performed by laser pyrolysis. The particles were produced using essentially the laser pyrolysis apparatus of Fig. 2, described above, using the reactant delivery apparatus of Fig. 4A.

The manganese chloride (Alfa Aesar, Inc., Ward Hill, MA) precursor and lithium chloride (Alfa Aesar, Inc.) precursor were dissolved into deionized water. The aqueous solution had a concentration of 4 molar LiCl and 4 molar MnCl<sub>2</sub>. The aqueous solution with the two metal precursors was carried into the reaction chamber as an aerosol. C<sub>2</sub>H<sub>4</sub> gas was used as a laser absorbing gas, and Argon was used as an inert gas. O<sub>2</sub>, Ar and C<sub>2</sub>H<sub>4</sub> were delivered into the gas supply tube of the reactant supply system. The reactant mixture containing MnCl<sub>2</sub>, LiCl, Ar, O<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> was introduced into the reactant nozzle for injection into the reaction chamber. The reactant nozzle had an opening with dimensions of 5/8 in. x 1/16 in. Additional parameters of the laser pyrolysis synthesis relating to the particles of Example 1 are specified in Table 5.

TABLE 5

	1
Crystal Structure	Amorphous
Pressure (Torr)	450
Argon-Window (SCCM)	700
Argon-Shielding (SLM)	5.6
Ethylene (SLM)	1.27
Argon (SLM)	1.46
Oxygen (SLM)	1.07
Laser Output (Watts)	590
Li Precursor	4 M Lithium Chloride

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Mn Precursor	4 M Manganese Chloride
Precursor Temperature °C	Room Temperature

sccm = standard cubic centimeters per minute

5 slm = standard liters per minute

Argon - Win. = argon flow through inlets 216, 218

Argon - Sld. = argon flow through annular channel 142.

Argon = Argon directly mixed with the aerosol

The production rate of manganese oxide/  
10 lithium manganese oxide particles was typically about 1  
g/hr. To evaluate the atomic arrangement, the samples  
were examined by x-ray diffraction using the Cu(K $\alpha$ )  
radiation line on a Siemens D500 x-ray diffractometer.  
X-ray diffractograms for a sample produced under the  
15 conditions specified in Table 5 is shown in Fig. 37.  
The x-ray diffractogram shown in Fig. 37 indicates that  
the sample was amorphous. In particular, a broad peak  
from about 27° to about 35° corresponds to the amorphous  
lithium manganese oxide. A sharp peak at about 15° is  
20 due to the presence of a trace amount of manganese  
chloride contamination. A sharp peak at 53° is due to  
a trace amount of an unidentified contaminant.

Example 6 - Heat Treatment of Lithium Manganese Oxide  
Particles Produced by Laser Pyrolysis

25 A sample of manganese oxide/lithium manganese  
oxide nanoparticles produced by laser pyrolysis  
according to the conditions specified in the Example 5  
were heated in an oven under oxidizing conditions. The  
oven was essentially as described above with respect to  
30 Fig. 22. Between about 100 and about 300 mg of  
nanoparticles were placed in an open 1 cc vial within  
the quartz tube projecting through the oven. Oxygen gas  
was flowed through a 1.0 inch diameter quartz tube at a  
flow rate of 308 cc/min. The oven was heated to about  
35 400°C. The particles were heated for about 16 hours.

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The crystal structure of the resulting heat treated particles were determined by x-ray diffraction. The x-ray diffractogram for heated sample is shown in Fig. 38. The x-ray diffractogram shown in Fig. 38 indicates that the collection of particles involved mixed phase material with major components of  $\text{LiMn}_2\text{O}_4$  (about 60% by volume) and  $\text{Mn}_3\text{O}_4$  (about 30% by volume) and a minor component of  $\text{Mn}_2\text{O}_3$  (about 10% by volume). The  $\text{LiMn}_2\text{O}_4$  compound has a cubic spinel crystal structure. It is possible that the sample included additional amorphous phases of materials. In particular, based on the amount of lithium introduced in the reactant stream, the sample presumably contains additional lithium that is not identified in the crystalline phases.

Example 7 - Lithium Incorporation Into Manganese Oxide Particles

Manganese oxide particles produced as described in Example 4 were further treated to form lithium manganese oxide. The manganese oxide particles used were a mixture of particles formed under the conditions for the synthesis specified in columns 1 and 2 of Table 4. About 2.0 grams of nanocrystalline manganese oxide was mixed with about 1.2 grams of lithium nitrate,  $\text{LiNO}_3$  (Alfa Aesar, Inc., Ward Hill, MA). The mixtures were heated in an oven under either pure  $\text{O}_2$  or under pure Ar. The oven was essentially as described above with respect to Fig. 22B. The mixture of nanocrystalline manganese oxide and lithium nitrate were placed in an alumina boat within the quartz tube projecting through the oven. The selected gas was flowed through a 1.0 inch diameter quartz tube at a flow rate of about 40 cc/min. The oven was heated to about 400°C. The particles were heated for about 16 hours.

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Three samples were treated. The first sample had a weight ratio of 1.84 parts nanocrystalline MnO to 1 part LiNO<sub>3</sub>. The second sample had a weight ratio of 1.66 parts nanocrystalline MnO to 1 part LiNO<sub>3</sub>. Samples 1 and 2 were heat treated under a flow of oxygen gas. Sample 3 had a weight ratio of 1.63 parts nanocrystalline MnO to 1 part LiNO<sub>3</sub>. Sample 3 was heat treated under a flow of argon gas.

To evaluate the crystal structure of the materials following heat treatment, the samples were examined by x-ray diffraction using the Cu(K $\alpha$ ) radiation line on a Siemens D5000 x-ray diffractometer. The x-ray diffraction spectra for samples 1-3 are depicted in Fig. 39. The spectrum for sample 1 has peaks corresponding to unreacted manganese oxide. By decreasing the manganese oxide to lithium nitrate ratio from 1.84 to 1.66, complete reaction of the manganese oxide was observed. The lithium manganese oxide of sample 2 had a lattice parameter of approximately 8.17 Å, which is similar to that of defect spinel Li<sub>2</sub>Mn<sub>4</sub>O<sub>9</sub>. The lithium manganese oxide of sample 3 had a lattice parameter of approximately 8.23 Å, which is similar to the lattice parameter of LiMn<sub>2</sub>O<sub>4</sub>.

Transmission electron microscopy (TEM) was used to determine particle sizes and morphology of the lithium manganese oxide and the manganese oxide starting materials. A TEM micrograph for the manganese oxide nanoparticle starting material is shown in Fig. 40. A TEM micrograph for the lithium manganese oxide of sample 1 is shown in Fig. 41. Note that the particle size did not change significantly, if at all, during the heating process. Due to the lack of optimization of the aerosol conditions, the particles of manganese oxide displayed in Fig. 40 have a broader particle size distribution

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than found for manganese oxide in Examples 1 and 2 above. Since the incorporation of lithium into the manganese oxide nanoparticles does not significantly change the size of the particles, lithium manganese oxide nanoparticles with a narrow size distribution can be made using the manganese oxide nanoparticles described above.

Example 8 - Direct Laser Pyrolysis Synthesis of Crystalline Lithium Manganese Oxide With an Aerosol

The synthesis of crystalline lithium manganese oxide particles described in this example was performed by laser pyrolysis. The particles were produced using essentially the laser pyrolysis apparatus of Fig. 2, described above, using the reactant delivery apparatus of Fig. 4B or 4C.

Two solutions were formed with manganese nitrate ( $\text{Mn}(\text{NO}_3)_2$ , Alfa Aesar, Inc., Ward Hill, MA) precursor, lithium nitrate (Alfa Aesar, Inc.) precursor and urea ( $\text{CH}_4\text{N}_2\text{O}$ ). The first solution was used to form sample 3 of Table 6. The first solution was an aqueous solution with a concentration of 3 molar  $\text{LiNO}_3$  and 4 molar  $\text{Mn}(\text{NO}_3)_2$ . The solvent for the second solution was a 50:50 percent by weight mixture of isopropyl alcohol and deionized water. The second solution had a concentration of 2 molar  $\text{LiNO}_3$ , 2 molar  $\text{Mn}(\text{NO}_3)_2$ , and 3.6 molar urea. The second solution was used to form the first and second samples of Table 6.

The selected solution with the two metal precursors was carried into the reaction chamber as an aerosol.  $\text{C}_2\text{H}_4$  gas was used as a laser absorbing gas, and Argon was used as an inert gas.  $\text{O}_2$ , Ar and  $\text{C}_2\text{H}_4$  were delivered into the gas supply tube of the reactant supply system. The reactant mixture containing  $\text{Mn}(\text{NO}_3)_2$ ,  $\text{LiNO}_3$ , Ar,  $\text{O}_2$  and  $\text{C}_2\text{H}_4$  was introduced into the

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reactant nozzle for delivery into the reaction chamber. The reactant nozzle had an opening with dimensions of 5/8 in. x 1/4 in. The first two samples were formed with a reactant delivery system essentially as shown in Fig. 4B. The third sample was prepared with a reactant delivery system essentially as shown in Fig. 4C. Additional parameters of the laser pyrolysis synthesis relating are specified in the first two columns of Table 6.

10

TABLE 6

15

20

	1	2	3
Crystal Structure	LiMn <sub>2</sub> O <sub>4</sub> (major) + Mn <sub>3</sub> O <sub>4</sub>	LiMn <sub>2</sub> O <sub>4</sub> (major) + Mn <sub>3</sub> O <sub>4</sub>	LiMn <sub>2</sub> O <sub>4</sub> (major) + Mn <sub>3</sub> O <sub>4</sub>
Pressure (Torr)	600	600	600
Argon-Window (SLM)	2.24	2.24	2.24
Argon-Shielding (SLM)	9.86	9.86	9.86
Ethylene (SLM)	0.80	0.80	1.24
Argon (SLM)	3.61	3.60	4.17
Oxygen (SLM)	0.97	0.99	1.46
Laser Input (Watts)	650	970	380
Laser Output (Watts)	540	830	320
Production Rate (gm/hr)	1.8	1.3	17.0
Precursor Temperature °C	Room Temp.	Room Temp.	Room Temp.

25

slm = standard liters per minute  
 Argon - Win. = argon flow through inlets 216, 218  
 Argon - Sld. = argon flow through annular channel 142.  
 Argon = Argon directly mixed with the aerosol

30

To evaluate the atomic arrangement, the samples were examined by x-ray diffraction using the Cu(K $\alpha$ ) radiation line on a Siemens D500 x-ray diffractometer. X-ray diffractograms for samples produced under the conditions of columns 1 and 2 specified in Table 6 are shown in Fig. 42. This is a



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representative diffractogram, although some samples had relatively small peaks due to  $\text{Mn}_2\text{O}_3$  contamination. X-ray diffraction peaks characteristic of spinel lithium manganese oxide are clearly visible in the diffractogram. Small differences in stoichiometry within the spinel structure are difficult to elucidate from the x-ray diffractogram. In addition, the x-ray diffractogram peaks are broad, which may be due to the small particle size or inhomogeneous broadening resulting from either having a mixed phase material or variations in stoichiometry. Nevertheless, the diffractogram is consistent with the sample containing a mixture of  $\text{LiMn}_2\text{O}_4$  and  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  or an intermediate stoichiometry material. These conclusions are confirmed by electrochemical evaluation described below. In any case, the crystalline lithium manganese oxide seems to comprise a majority (greater than about 50%) of the material in one form or another.

Transmission electron microscopy (TEM) was used to determine particle sizes and morphology of the as synthesized, crystalline lithium manganese oxide. A TEM micrograph for the lithium manganese oxide of the sample produced under the conditions of column 2 of Table 6 is shown in Fig. 43. The corresponding particle size distribution is shown in Fig. 44. The particle size distribution was obtained following the procedure described in Example 1. The average particle diameter is about 40 nm. The particle size distribution shows a relatively broad particle size distribution relative to particle size distributions generally obtainable by laser pyrolysis. Reactant delivery with the reactant delivery apparatus of Fig. 4C has a higher reactant throughput and a correspondingly larger production rate compared with the aerosol delivery apparatuses of Figs.

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4A and 4B. The aerosol produced by the Apparatus of Fig. 4C evidently is not as uniform as the aerosols produced by the other two apparatuses. The particle size distribution using the reactant delivery apparatus of Fig. 4C can be narrowed by using a lower pressure from about 200-300 Torr and by increasing the O<sub>2</sub> flow to obtain the desired phase of product.

#### Example 9 - Silver Vanadium Oxide Nanoparticles

The synthesis of silver vanadium oxide nanoparticles described in this example was performed by laser pyrolysis. The particles were produced using essentially the laser pyrolysis apparatus of Fig. 2, described above, using the reactant delivery apparatus of Fig. 4B or 4C.

Two solutions were prepared for delivery into the reaction chamber as an aerosol. Both solutions were produced with comparable vanadium precursor solutions. To produce the first vanadium precursor solution, a 10.0 g sample of vanadium (III) oxide (V<sub>2</sub>O<sub>3</sub>) from Aldrich Chemical (Milwaukee, WI) was suspended in 120 ml of deionized water. A 30 ml quantity of 70% by weight aqueous nitric acid (HNO<sub>3</sub>) solution was added dropwise to the vanadium (III) oxide suspension with vigorous stirring. Caution was taken because the reaction with nitric acid is exothermic and liberates a brown gas suspected to be NO<sub>2</sub>. The resulting vanadium precursor solution (about 150 ml) was a dark blue solution. The second vanadium precursor solution involved the scale-up of the first precursor solution by a factor of three in all ingredients.

To produce a first silver solution, a solution of silver carbonate (Ag<sub>2</sub>CO<sub>3</sub>) from Aldrich Chemical (Milwaukee, WI) was prepared by suspending 9.2 g of silver carbonate in a 100 ml volume of deionized water.

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A 10 ml quantity of 70% by weight aqueous nitric acid ( $\text{HNO}_3$ ) was added dropwise with vigorous stirring. A clear colorless solution resulted upon completion of the addition of nitric acid. To produce a first metal mixture solution for aerosol delivery, the silver solution was added to the first vanadium precursor solution with constant stirring. The resulting dark blue first metal mixture solution had a molar ratio of vanadium to silver of about 2:1.

To produce a second silver solution, 34.0 g of silver nitrate ( $\text{AgNO}_3$ ) from Aldrich Chemical (Milwaukee, WI) was dissolved in a 300 ml volume of deionized water. To prepare a second solution of metal mixtures for aerosol delivery, the silver nitrate solution was added to the second vanadium precursor solution with constant stirring. The resulting dark blue second metal mixture solution also had a molar ratio of vanadium to silver of about 2:1.

The selected aqueous solution with the vanadium and silver precursors was carried into the reaction chamber as an aerosol.  $\text{C}_2\text{H}_4$  gas was used as a laser absorbing gas, and Argon was used as an inert gas.  $\text{O}_2$ , Ar and  $\text{C}_2\text{H}_4$  were delivered into the gas supply tube of the reactant supply system. The reactant mixture containing vanadium oxide, silver nitrate, Ar,  $\text{O}_2$  and  $\text{C}_2\text{H}_4$  was introduced into the reactant nozzle for injection into the reaction chamber. The reactant nozzle had an opening with dimensions of 5/8 in. x 1/4 in. Additional parameters of the laser pyrolysis synthesis relating to the particle synthesis are specified in Table 7. Sample 1 was prepared using the reactant delivery system essentially as shown in Fig. 4B while sample 2 was prepared using the reactant delivery system essentially as shown in Fig. 4C.

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TABLE 7

	1	2
Crystal Structure	Mixed Phase	Mixed Phase
Pressure (Torr)	600	600
Argon-Window (SLM)	2.00	2.00
Argon-Shielding (SLM)	9.82	9.86
Ethylene (SLM)	0.74	0.81
Argon (SLM)	4.00	4.80
Oxygen (SLM)	0.96	1.30
Laser Power (input) (Watts)	490-531	390
Laser Power (output) (Watts)	445	320
Precursor Solution	1	2
Precursor Temperature °C	Room Temperature	Room Temperature

slm = standard liters per minute

Argon - Win. = argon flow through inlets 216, 218

Argon - Sld. = argon flow through annular channel 142.

Argon = Argon directly mixed with the aerosol

To evaluate the atomic arrangement, the samples were examined by x-ray diffraction using the Cu(K $\alpha$ ) radiation line on a Siemens D500 x-ray diffractometer. X-ray diffractograms for samples 1 (lower curve) and 2 (upper curve) produced under the conditions specified in Table 7 are shown in Fig. 45. The samples had peaks corresponding to VO<sub>2</sub>, elemental silver and peaks that did not correspond to known materials. A significant crystalline phase for these samples had peaks at 2 $\theta$  equal to about 30-31°, 32, 33 and 35. This phase is thought to be a previously unidentified silver vanadium oxide phase. This crystalline silver vanadium oxide phase is observed in samples prepared by mixing vanadium oxide nanoparticles and silver nitrate under conditions where the samples

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are heated for an insufficient time period to produce  $\text{Ag}_2\text{V}_4\text{O}_{11}$ . Specific capacity measurements of sample 1 in a coin cell are consistent with this interpretation.

Powders of samples produced under the conditions specified in Table 7 were further analyzed using transmission electron microscopy. The TEM micrographs are shown in Figs. 46A (first column of Table 7) and 46B (second column of Table 7). The TEM micrograph has a particles falling within different size distributions. This is characteristic of mixed phase materials made by laser pyrolysis, where each material generally has a very narrow particle size distribution. The portion of silver vanadium oxide in the mixed phase material should be increased by an increase in oxygen flow, a decrease in laser power and an increase in pressure. The production of silver vanadium oxide particle by laser pyrolysis is described further in U.S. Patent Application Serial No. 09/311,506 to Reitz et al., entitled "Metal Vanadium Oxide Particles," incorporated herein by reference.

#### BATTERY EXAMPLES

In addition, lithium manganese oxide based lithium batteries were evaluated to determine the charge capacity and energy density of the lithium manganese oxide powders used as active materials in the positive electrodes. The batteries tested in examples 9-11 were all produced following a common procedure. The lithium manganese oxide powders (LMO) were mixed with a conductive acetylene black powder (AB) (Catalog number 55, Chevron Corp.) at a ratio of 80:10. The powder mixture was ground with a mortar and pestle to thoroughly mix the powders.

A few drops of polytetrafluoroethylene (PTFE) solution were added to the homogeneous powder mixture.

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The 10 percent PTFE solution included PTFE (Aldrich Chemical Co., Milwaukee, WI) solution in water. The final ratio of LMO:AB:PTFE was 80:10:10. A small amount of methyl alcohol (Aldrich Chemical Co., Milwaukee, WI) was added to the mixture. In addition, isopropyl alcohol (Aldrich Chemical Co., Milwaukee, WI) was added to cover the mixture.

The slurry was put in a blender to mix thoroughly, and the solution was passed through a vacuum filter to remove the solvents. The resulting powder mixture was needed and rolled to a 5-mil thickness. An aluminum mesh (Dekler, Branford CT) was placed on the mixture, and further rolled down to achieve a final thickness with the mesh of 5 mils. The mixture with the aluminum mesh was baked in a vacuum oven for two hours at 250°C to remove residual solvent and to melt the PTFE. After removal from the oven, the electrodes were punched to 16mm and pressed at 5000lbs of pressure. The punched out electrodes were placed again in the vacuum oven overnight at 120°C to remove residual moisture. After removal from the oven, the electrodes were immediately placed in a glove box (Vacuum Atmosphere Co., Hawthorne, CA) under an argon atmosphere. In the glove box, the electrodes were weighted and measured for thickness.

The samples were tested in an cell 800 with an airtight two-electrode configuration shown in Fig. 47. The casing 802 for the sample battery was obtained from Hohsen Co., Osaka, Japan. The casing included a top portion 804 and a bottom portion 806, which are secured with four screws 808. The two other screws not shown in Fig. 44 are behind the two screws shown. Lithium metal (Alfa/Aesar, Ward Hill, MA) was used as a negative electrode 812. Negative electrode 812 was placed within

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the bottom portion 806. A separator 814, Celgard® 2400 (Hoechst Celanese, Charlotte, NC), was placed above the lithium metal. A Teflon® ring 816 was placed above separator 814. A positive electrode 818 was placed mesh  
5 side up within Teflon® ring 816. An aluminum pellet 820 was placed above positive electrode 818, and electrolyte was added. The electrolyte from EM Industries (Hawthorne, NY) was 1M LiPF<sub>6</sub> in 1:1 ethylene carbonate/dimethyl carbonate. A Teflon® o-ring is located between  
10 top portion 804 and bottom portion 806 to electrically insulate the two electrodes. Similarly, screws 808 are placed within a Teflon® sleeve to electrically insulate screws 808 from top portion 804 and bottom portion 806. Electrical contact between the battery tester and cell  
15 800 is made by way of top portion 804 and bottom portion 806.

The samples were tested with a discharge/charge rate at a constant current of 0.5 mA/cm<sup>2</sup>, and cycled between 2.5V to 4.4V, or 2.2V to 3.3V, or 3.5V to  
20 4.4V at 25°C. The measurements were controlled by an Arbin Battery Testing System, Model BT4023, from Arbin Instruments, College Station, TX. The charging/discharging profiles were recorded, and the discharge capacity of the active material was obtained.

25 The energy density is evaluated by the integral over the discharge time of the voltage multiplied by the current divided by the mass of the active material. The current during testing was 1mA, corresponding to a current density of 0.5 mA/cm<sup>2</sup>. The  
30 active material mass ranged from about 30 to about 50 mg.

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Example 10 - Four Volt Cycling Behavior - Thermal  
Synthesis of Lithium Manganese Oxide

This example explores the four volt cycling behavior of four different lithium manganese oxide materials. Cells were produced following the procedure outlined above with material produced as sample 2 and sample 3 of Example 7. For comparison, cells were also produced using standard  $\text{LiMn}_2\text{O}_4$  and  $\text{Li}_2\text{Mn}_4\text{O}_9$ . Commercial  $\text{LiMn}_2\text{O}_4$  was purchased from Alfa Aesar, a Johnson Matthey Company, Ward Hill, MA.  $\text{Li}_2\text{Mn}_4\text{O}_9$  (standard  $\text{Li}_2\text{Mn}_4\text{O}_9$ ) was synthesized using a standard procedure based on heating a mixture of manganese carbonate and lithium carbonate at about  $400^\circ\text{C}$  for about 60 hours. The cycling behavior in the four volt range was examined by charging the material to a voltage of 4.40 volts and allowing the material to discharge. The resulting discharge curve is shown in Fig. 48. In Fig. 48, the cycling behavior of cells made with nanoparticles from Example 7 are labelled sample 2 and sample 3, appropriately, and the cycling behavior of cells made with the commercial or standard powders are labelled by their stoichiometry with the notation "Commercial". Note that the cell with sample 2 had a discharge curve similar to the  $\text{Li}_2\text{Mn}_4\text{O}_9$  commercial material, and the cell with sample 3 had a discharge curve similar to  $\text{LiMn}_2\text{O}_4$  commercial material.

Example 11 - Three Volt Cycling Behavior - Thermal  
Synthesis of Lithium Manganese Oxide

This example explores the three volt cycling behavior of four different lithium manganese oxide materials. Cells were produced following the procedure outlined above with material produced as sample 2 and sample 3 of Example 7. For comparison, cells were also produced using commercial  $\text{LiMn}_2\text{O}_4$  and  $\text{Li}_2\text{Mn}_4\text{O}_9$ . The cycling behavior in the three volt range was examined by



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charging the material to a voltage of 3.30 volts and allowing the material to discharge. The resulting discharge curve is shown in Fig. 49. In Fig. 49, the cycling behavior of cells made with nanoparticles from Example 7 are labelled sample 2 and sample 3, appropriately, and the cycling behavior of cells made with the commercial powders are labelled by their stoichiometry with the notation "Commercial". Note that the cell with sample 2 had an insertion potential similar to the  $\text{Li}_2\text{Mn}_4\text{O}_9$  commercial material, and the cell with sample 3 had a insertion potential similar to  $\text{LiMn}_2\text{O}_4$  commercial material.

Example 12 - Cycling Properties - Thermal Synthesis of Lithium Manganese Oxide

The cycling behavior of cells made as described above was explored further for four different positive electrode materials. Cells were produced following the procedure outlined above with material produced as sample 2 and sample 3 of Example 7. For comparison, cells were also produced using commercial  $\text{LiMn}_2\text{O}_4$  and  $\text{Li}_2\text{Mn}_4\text{O}_9$ . Cells with positive electrode materials from sample 2 and commercial  $\text{LiMn}_2\text{O}_4$  were produced and run in duplicates. Only one cell was produced with the sample 3 materials, while three cells with commercial  $\text{Li}_2\text{Mn}_4\text{O}_9$  were produced and run. For each cycle, the capacity in mAh/g were evaluated. The cells were cycled between about 3.3 volts and 2.0 volts. The results are plotted in Fig. 50.

The cycling results show that the cells produced with the nanoparticles have greater cycling stability. The improved cycling stability may be due to the nanoparticles being more structurally resistant to the repetitive volume expansion and contraction accompanying the lithium insertion and extraction.

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Thus, this data indicates an advantage of nano-scale lithium manganese oxide particles as a lithium based rechargeable battery active material.

Example 13 - Beaker Cell Testing of Lithium Manganese Oxide Directly Produced by Laser Pyrolysis Synthesis

5           The properties of crystalline lithium manganese oxide nanoparticles directly synthesized by laser pyrolysis was examined using a beaker cell test. Test cells were produced with two samples of  
10   nanomaterials. The first sample was produced under the conditions indicated in column 1 in Table 6 of Example 8, and the second sample was produced under the conditions indicated in column 2 in Table 6. Both samples had a majority component of  $\text{LiMn}_2\text{O}_4$  and a  
15   minority phase of  $\text{Mn}_3\text{O}_4$ .

          To produce the batteries for beaker cell testing, the lithium manganese oxide powders were mixed with a conductive acetylene black powder (Catalog number 55, Chevron Corp.) at a ratio of 60:30. The powder  
20   mixture was ground with a mortar and palette to thoroughly mix the powders.

          A few drops of polyvinylidene fluoride (PVDF) solution were added to the homogeneous powder mixture. The 10 percent PVDF solution included PVDF (type 714,  
25   Elf Atochem North America, Inc., Philadelphia, PA) dissolved in 1-methyl-2-pyrrolidinone (Aldrich Chemical Co., Milwaukee, WI). The final ratio of  $\text{Li}_x\text{Mn}_y\text{O}_z$ :AB:PVDF was 60:30:10. The resulting slurry was spread onto a preweighed aluminum metal mesh. The mesh with the  
30   slurry was baked in a vacuum oven overnight at  $120^\circ\text{C}$  to remove the solvent and residual moisture. After removal from the oven, the electrodes were immediately placed in a glove box (Vacuum Atmosphere Co., Hawthorne, CA) under an argon atmosphere and weighted again.

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All discharge/charge experiments were conducted in the glove box. The water and oxygen concentrations in the glove box were measured to be less than 1 ppm and 1.5 ppm, respectively. The samples were  
5 tested in a three electrode configuration, as shown in Fig. 51. In the test set up, cathode 832 on aluminum mesh 834 is placed in container 836. Container 836 holds liquid electrolyte 838. Counter electrode 840 and reference electrode 842 are also placed into container  
10 836. Lithium metal was used as both counter electrode and reference electrode. The electrodes are connected to a battery testing system 844.

No separator is needed for this testing configuration since the electrodes are physically  
15 separated. Alternatively, the liquid electrolyte can be viewed as the separator. The liquid electrolyte (from Merck & Co., Inc.) was 1M LiClO<sub>4</sub> in propylene carbonate.

Charge and discharge experiments were conducted at an approximately constant current  
20 equivalent to about 5 mA per gram of oxide within the electrode. Each electrode contained about 10 mg of nanoparticles. Thus, the currents were about 0.05 mA. If the material were pure lithium manganese oxide, this charge/discharge rate corresponds to a rate of C/30  
25 (i.e., a rate such that the cathode would be fully discharged in 30 hours). The cells were initially charged from their open-circuit voltage up to 4.4 volts and then discharged down to 2.0 volts.

The measurements were controlled by an Arbin  
30 Battery Testing System, Model BT4023, from Arbin Instruments, College Station, TX. The charging/discharging profiles were recorded, and the specific capacity was obtained. The specific capacity was evaluated as the discharge capacity divided by the mass

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of the active material. Also, the differential capacity ( $\delta x/\delta V$ ) was determined by taking the derivative of the discharge capacity with respect to voltage. Therefore, the differential capacity is the inverse slope of the charge and discharge profile with respect to voltage. Peaks in the plot of differential capacity versus voltage indicate voltages where lithium inserts into the host material. In a lithium metal cell, the cell voltage is approximately proportional to the chemical potential of  $\text{Li}^+$  in the host material. Therefore, the differential capacity can be used to characterize and/or identify the material and its structure.

In Fig. 52, the discharge curves for samples 1 and 2 are compared with the discharge curve for bulk commercial  $\text{LiMn}_2\text{O}_4$ . While the laser pyrolysis synthesized lithium manganese oxide had a significantly lower specific capacity, the nanoparticles exhibited significant specific capacities. The differential capacity of the nanoparticles and the bulk/commercial materials, shown in Fig. 53, had similar peak position and shape. This indicates that the electrochemically active phases of all three materials have nearly identical insertion profiles. Thus, the crystal structure of the three materials was the same. The lower specific capacities of the nanomaterials can be attributed to phases that are not electrochemically active in this test, including the manganese oxide material and lithium that has not been incorporated into lithium manganese oxide.

The embodiments described above are intended to be illustrative and not limiting. Additional embodiments are within the claims below. Although the present invention has been described with reference to preferred embodiments, workers skilled in the art will

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recognize that changes may be made in form and detail without departing from the spirit and scope of the invention.

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WHAT IS CLAIMED IS:

1. A collection of particles comprising manganese oxide, the collection of particles having an average diameter less than about 500 nm, the manganese oxide having a structure selected from the group consisting of amorphous manganese oxide, crystalline MnO, crystalline  $\text{Mn}_5\text{O}_8$  and crystalline  $\text{Mn}_2\text{O}_3$ .
2. The collection of particles of claim 1 wherein the collection of particles have an average diameter from about 5 nm to about 250 nm.
3. The collection of particles of claim 1 wherein the collection of particles have an average diameter from about 5 nm to about 100 nm.
4. The collection of particles of claim 1 wherein the collection of particles have an average diameter from about 5 nm to about 50 nm.
5. The collection of particle of claim 1 wherein the particles comprise crystalline MnO.
6. The collection of particles of claim 1 wherein the particles comprise crystalline  $\text{Mn}_2\text{O}_3$ .
7. The collection of particles of claim 1 wherein the particles comprise crystalline  $\text{Mn}_5\text{O}_8$ .
8. The collection of particles of claim 1 wherein effectively no particles have a diameter greater than about four times the average diameter of the collection of particles.
9. The collection of particles of claim 1 wherein the collection of particles have a distribution of particle sizes such that at least about 95 percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter.
10. A method of producing a metal oxide powder, the method comprising reacting an aerosol within a

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reaction chamber to form metal oxide particles, the aerosol comprising a metal precursor and the metal oxide particles having an average diameter less than about 500 nm.

11. The method of claim 10 wherein the metal oxide comprises manganese oxide.

12. The method of claim 10 wherein the metal precursor comprises a compound selected from the group consisting of  $\text{MnCl}_2$  and  $\text{MnNO}_3$ .

13. The method of claim 10 wherein the reaction is driven by heat absorbed from a laser beam.

14. The method of claim 10 wherein the reaction chamber has a cross section along a direction perpendicular to a reactant stream with a dimension along a major axis greater than a factor of about two larger than a dimension along a minor axis.

15. The method of claim 10 wherein the aerosol is generated by an ultrasonic aerosol generator.

16. The method of claim 10 wherein the aerosol is generated by a mechanical atomization aerosol generator.

17. The method of claim 10 wherein the reaction takes place in the presence of an oxygen source.

18. A method for altering the stoichiometry of a collection of manganese oxide particles, the method comprising heating manganese oxide particles in an oxidizing environment at a temperature less than about 600°C.

19. The method of claim 18 wherein the collection of manganese oxide particles have an average diameter from about 5 nm to about 500 nm.

20. A battery having a cathode comprising manganese oxide particles, said manganese oxide particles having an average diameter less than about 250 nm.

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21. A method of producing a composite metal oxide particles, the method comprising reacting an aerosol to form a powder of composite metal oxide particles with an average diameter less than about 1 micron, the aerosol comprising a first metal compound precursor and a second metal compound precursor.

22. The method of claim 21 wherein the composite metal oxide comprises lithiated manganese oxide.

23. The method of claim 21 wherein the composite metal oxide comprises lithiated vanadium oxide.

24. The method of claim 21 wherein a metal precursor comprises a compound selected from the group consisting of  $\text{MnCl}_2$  and  $\text{MnNO}_3$ .

25. The method of claim 21 wherein a metal precursor comprises a compound selected from the group consisting of  $\text{LiCl}$  and  $\text{Li}_2\text{NO}_3$ .

26. The method of claim 21 wherein a metal precursor comprises  $\text{VOCl}_2$ .

27. The method of claim 21 wherein the reaction is driven by heat absorbed from a light beam.

28. The method of claim 27 wherein the laser beam is generated by an infrared laser.

29. The method of claim 21 wherein the precursor comprises a third metal precursor.

30. The method of claim 21 wherein the reaction takes place in the presence of an oxygen source.

31. A method for producing lithium metal oxide, the method comprising pyrolyzing a reactant stream in a reaction chamber, the reactant stream comprising a lithium precursor, a non-lithium metal precursor, an oxidizing agent, and an infrared absorber, where the pyrolysis is driven by heat absorbed from a light beam.

32. The method of claim 31 wherein the reactant stream comprises an aerosol.



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33. The method of claim 32 wherein the aerosol comprises a solution with a metal compound and a lithium compound.

34. The method of claim 33 wherein the metal compound comprises a manganese compound.

35. A collection of particles comprising lithium manganese oxide, the collection of particles having an average diameter less than about 250 nm, wherein the collection of particles have a distribution of particle sizes in which at least about 95 percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter.

36. The collection of particles of claim 35 wherein the collection of particles have an average diameter from about 5 nm to about 25 nm.

37. The collection of particles of claim 35 wherein the lithium manganese oxide has an approximate stoichiometry of  $\text{LiMn}_2\text{O}_x$ , where  $x \geq 3.8$ .

38. The collection of particles of claim 35 wherein the lithium manganese oxide has a cubic spinel crystal structure.

39. The collection of particles of claim 35 wherein the collection of particles have a distribution of particle sizes such that at least about 95 percent of the particles have a diameter greater than about 60 percent of the average diameter and less than about 140 percent of the average diameter.

40. A method of making lithium manganese oxide particles comprising heating a mixture of manganese monoxide (MnO) particles and a lithium compound, the manganese monoxide particles having an average diameter less than about 250 nm.

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41. The method of claim 40 wherein the lithium compound comprises  $\text{LiNO}_3$ .

42. The method of claim 40 wherein the heating is performed at a temperature from about 200 to about 600°C.

43. The method of claim 40 wherein the heating is performed under an atmosphere comprising  $\text{O}_2$ .

44. The method of claim 40 wherein the lithium manganese oxide has a cubic spinel crystal structure.

45. A method of making lithium manganese oxide particles comprising heating a mixture of particles of a manganese oxide and a lithium compound, the particles of manganese oxide having an average diameter less than about 250 nm, wherein the resulting lithium manganese oxide particles have a distribution of particle sizes in which at least about 95 percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter.

46. The method of claim 45 wherein the heating is performed at a temperature from about 200°C to about 500°C.

47. The method of claim 45 wherein the manganese compound comprises a manganese oxide, with the manganese in an oxidation state from +2 to +4.

48. A battery comprising lithium manganese oxide particles having an average diameter less than about 250 nm, wherein the lithium manganese oxide particles have a distribution of particle sizes in which at least about 95 percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter.

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49. The battery of claim 48 wherein the lithium manganese oxide particles have an average diameter less than about 100 nm.

50. A battery comprising lithium manganese oxide, the battery having a four volt profile with a cycling stability within about 20 percent of initial values after 25 cycles.

51. A battery comprising lithium manganese oxide, the battery having an initial capacity greater than 120 mAh/g.

52. The battery of claim 51 wherein the battery has an initial capacity greater than about 125 mAh/g.

53. A collection of particles comprising lithium manganese oxide, the collection of particles having an average diameter less than about 250 nm, the lithium manganese oxide comprising  $\text{Li}_2\text{Mn}_4\text{O}_9$ .

54. The collection of particles of claim 53 wherein the collection of particles have a distribution of particle sizes such that at least about 95 percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter.

55. A collection of particles comprising lithium manganese oxide, the collection of particles having an average diameter less than about 250 nm, the lithium manganese oxide having a lattice parameter along axis a of no more than 8.23 angstroms.

56. A method of producing crystalline ternary particles comprising reacting a reactant stream comprising precursors including the three atoms of the product ternary particles, wherein the relative amounts of the three atoms in the reactant stream and the reaction conditions are selected to yield the crystalline ternary particles.

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57. The method of claim 56 wherein the crystalline ternary particles comprises greater than about 25 weight percent of the product particles.

58. The method of claim 56 wherein the crystalline ternary particles comprises greater than about 40 weight percent of the product particles.

59. The method of claim 56 wherein the crystalline ternary particles comprises greater than about 50 weight percent of the product particles.

60. The method of claim 56 wherein the crystalline ternary particles comprise a metal oxide with two metals.

61. The method of claim 60 wherein the metal oxide comprises a lithium metal oxide.

62. The method of claim 61 wherein the lithium metal oxide comprises a lithium manganese oxide.

63. The method of claim 56 wherein the reactant stream comprises an aerosol.

64. The method of claim 63 wherein the aerosol comprises two metal species.

65. The method of claim 56 wherein the reactant stream comprises molecular oxygen.

66. A method of producing crystalline lithium manganese oxide particles comprising reacting a reactant stream comprising a manganese precursor and a lithium precursor, wherein the reaction is driven by energy from electromagnetic radiation.

67. The method of claim 66 wherein the reactant stream comprises an aerosol.

68. The method of claim 67 wherein the aerosol is directed with a gas through an elongated inlet for delivery into a reaction chamber.

69. The method of claim 66 wherein the reactant stream further comprises a radiation absorbing gas.

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70. The method of claim 66 wherein the pyrolysis is performed with a carbon dioxide laser.

71. A collection of particles comprising a crystalline multiple metal oxide having an average particle diameter less than about 500 nm, wherein the lithium manganese oxide particles have a distribution of particle sizes in which at least about 95 percent of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter.

72. The collection of particles of claim 71 wherein the collection of particle have an average particle diameter less than about 100 nm.

73. The collection of particles of claim 71 wherein the collection of particle have an average particle diameter less than about 50 nm.

74. The collection of particles of claim 71 wherein effectively no particles have a diameter greater than about three times the average diameter of the collection of particles.

75. The collection of particles of claim 71 wherein the collection of particles comprises at least about 40 percent by weight of the crystalline ternary particles.

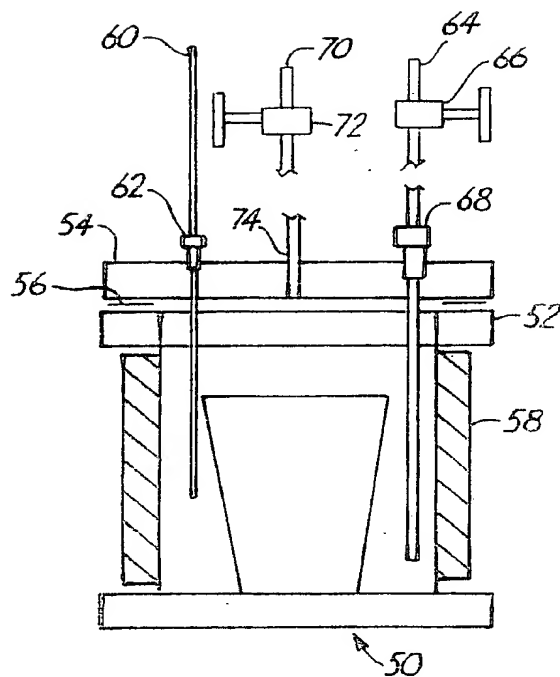


FIG. 1

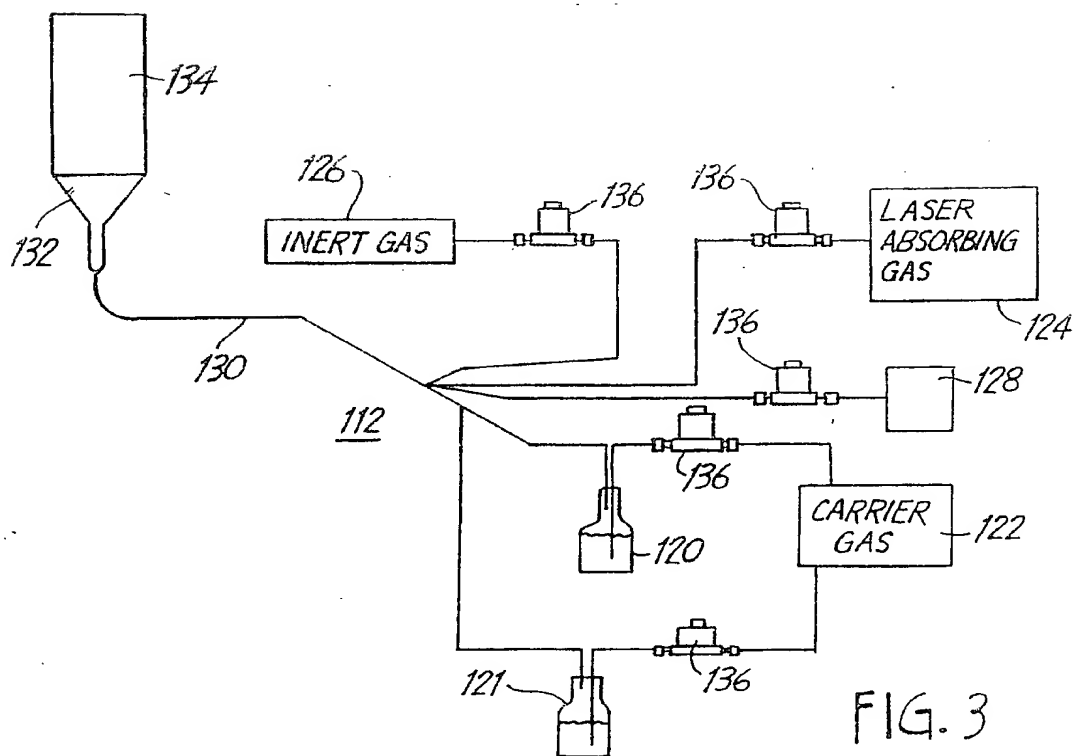
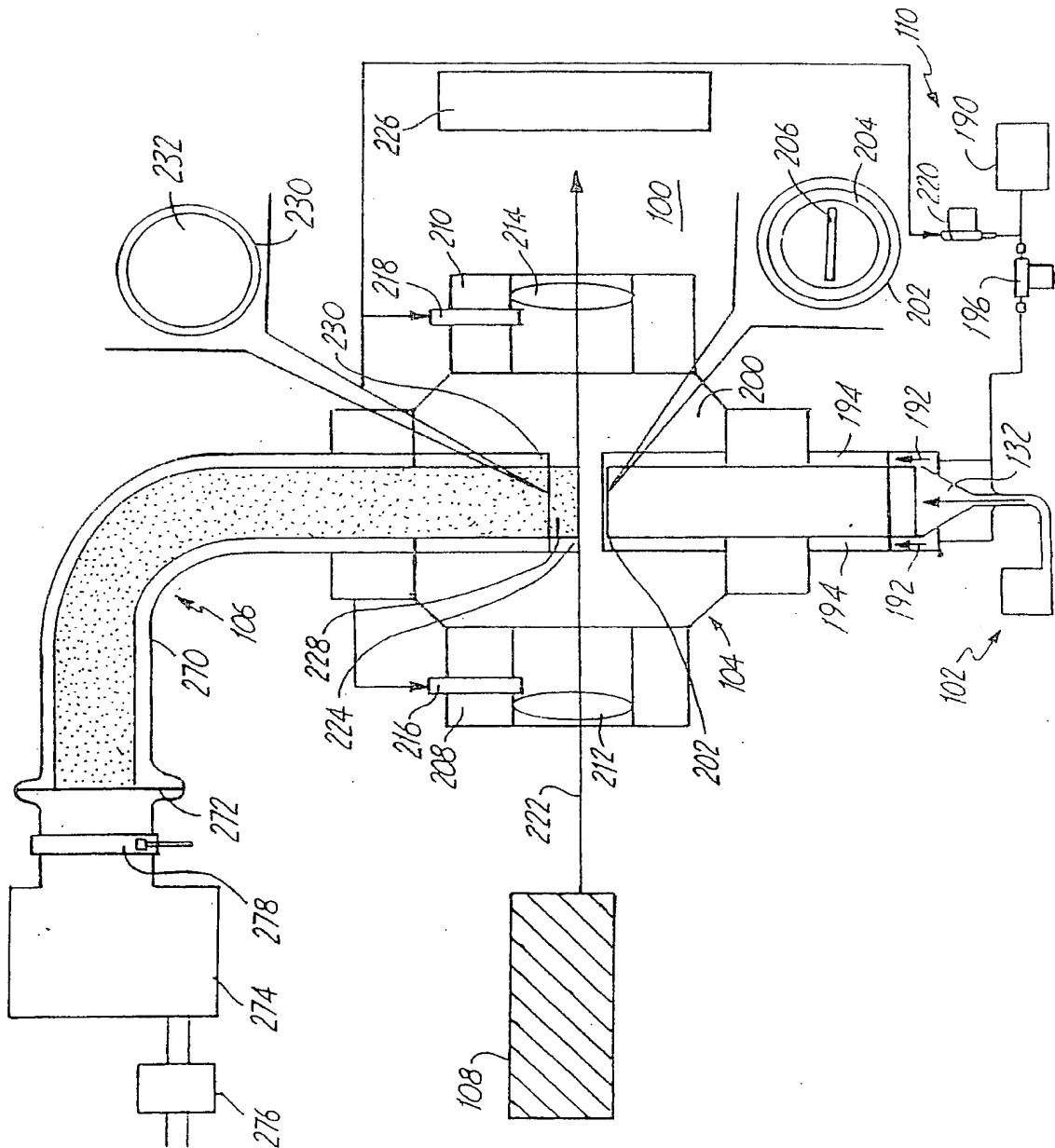
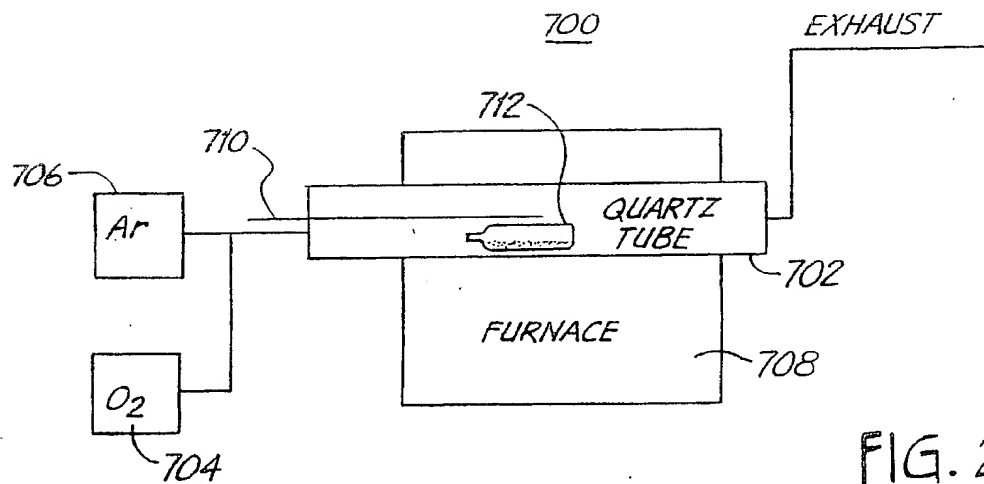
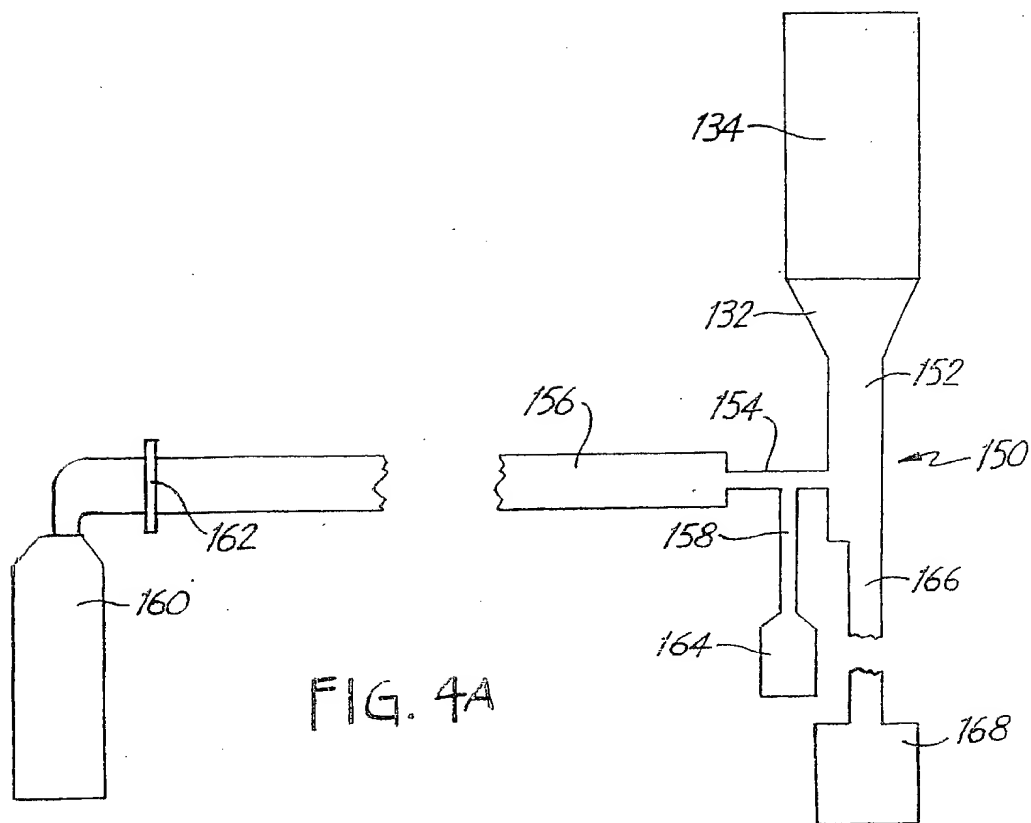


FIG. 3

FIG. 2







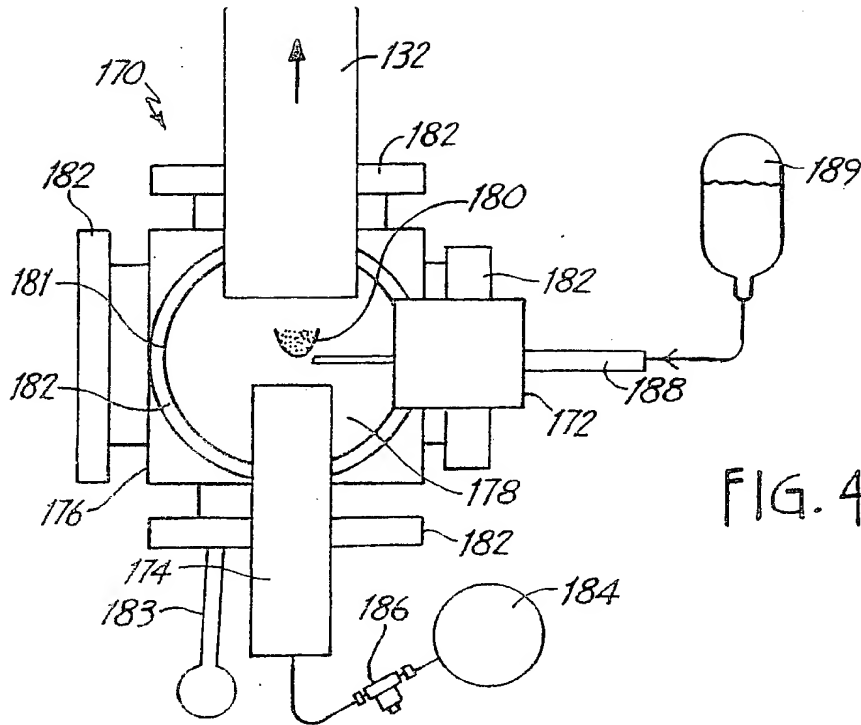


FIG. 4B

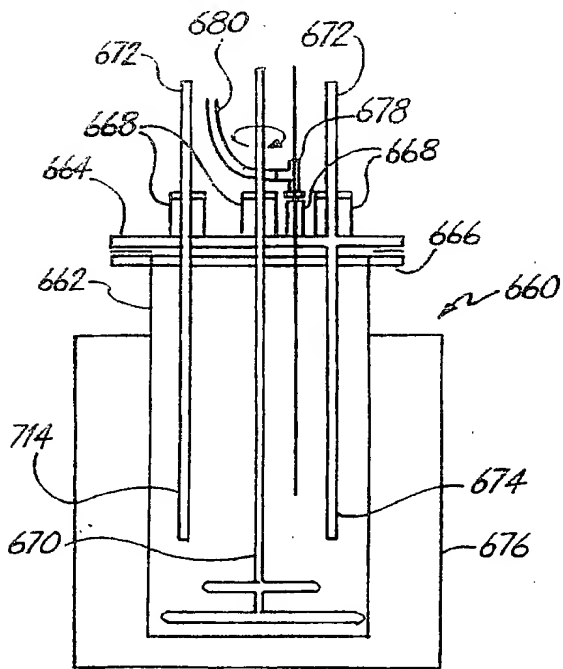


FIG. 22A

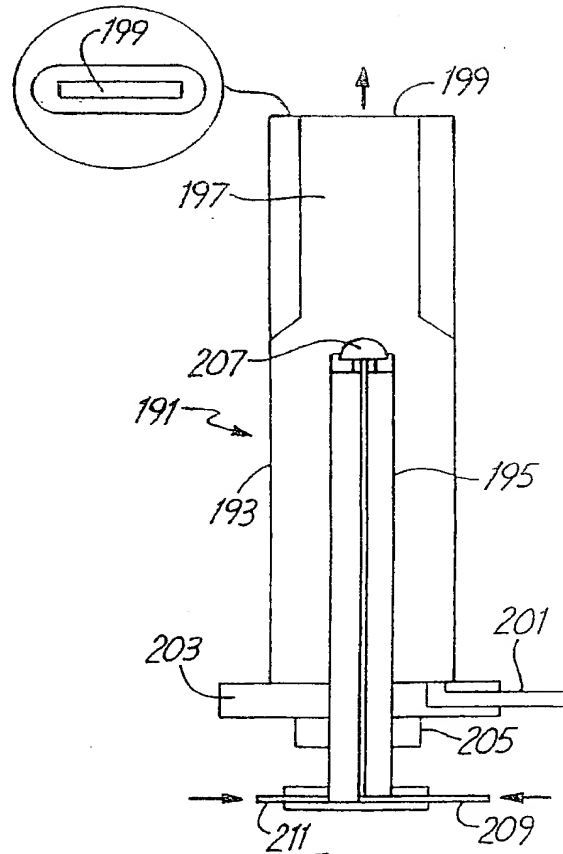
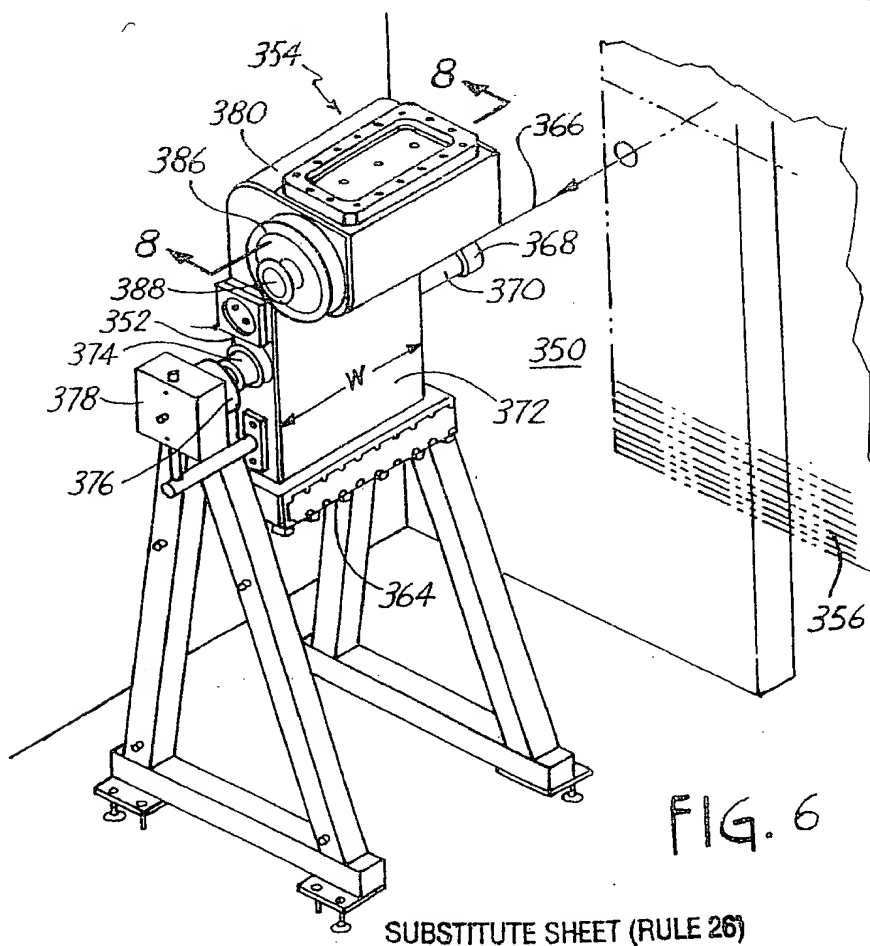
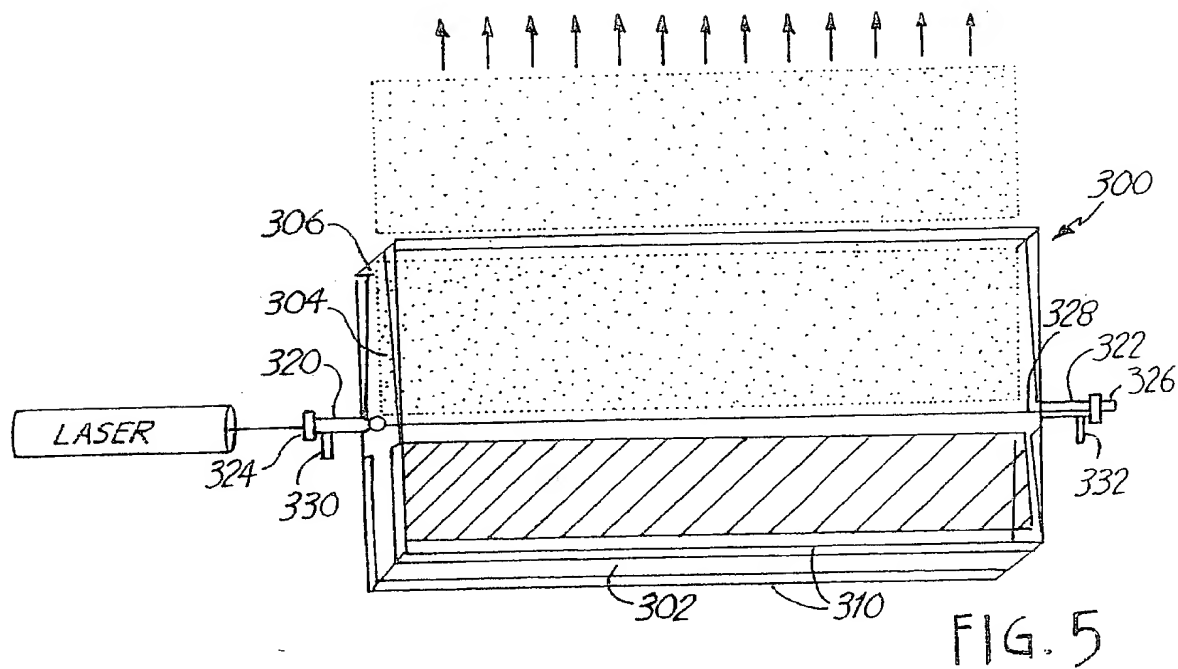


FIG. 4C



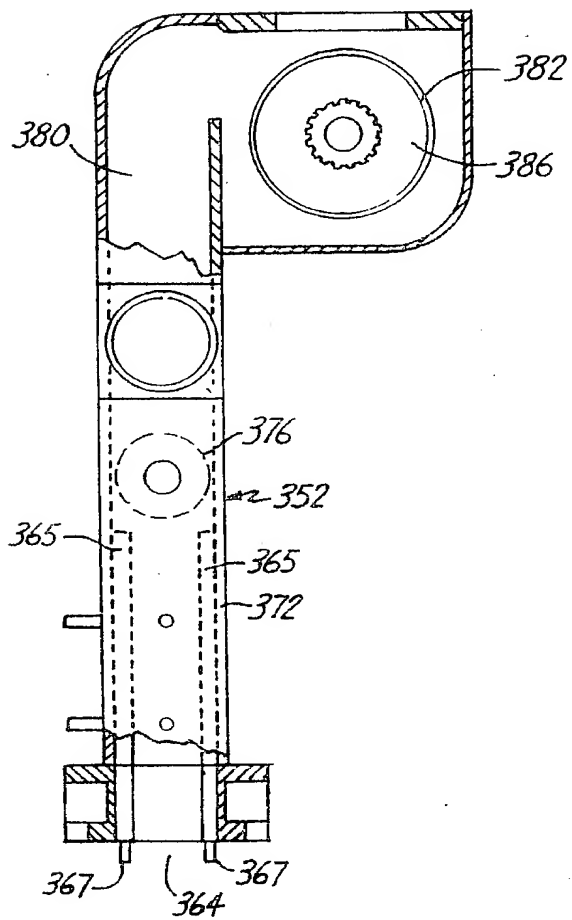


FIG. 7

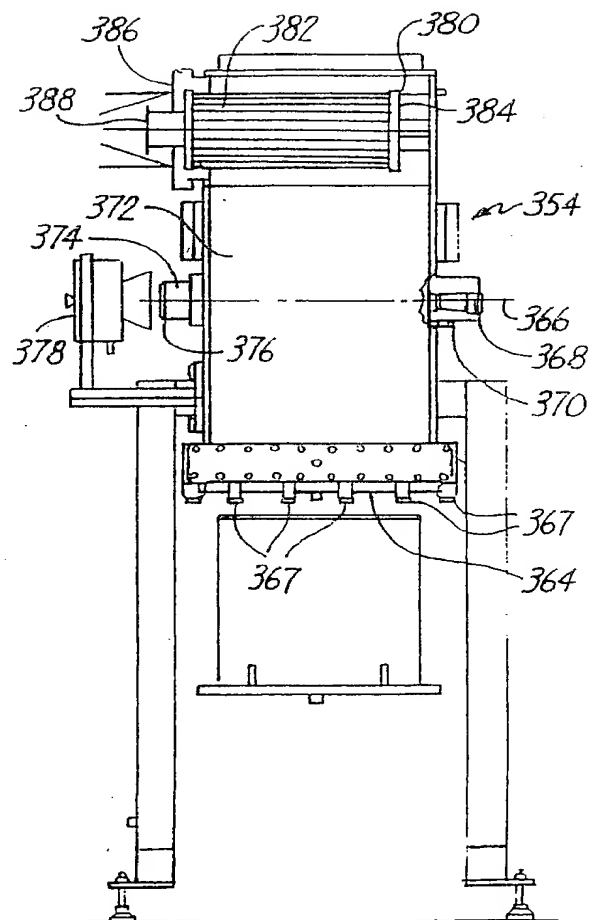
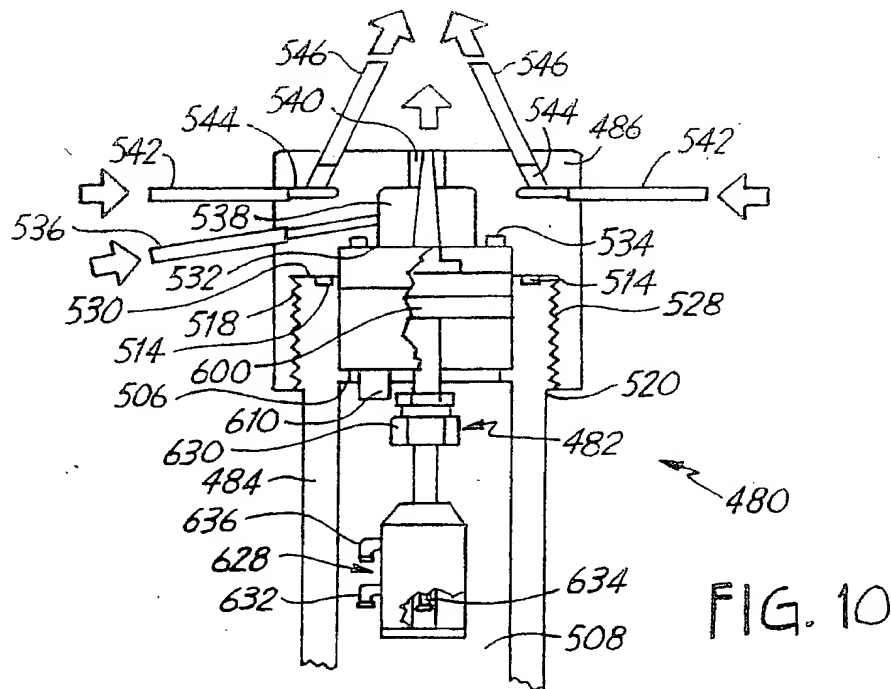
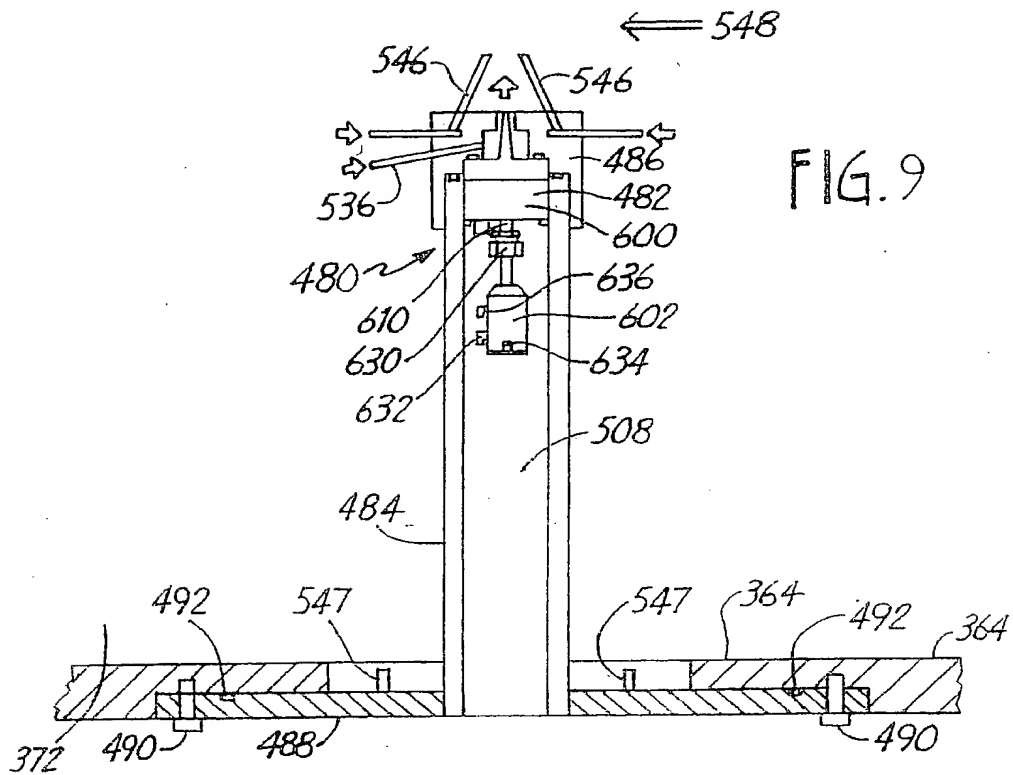
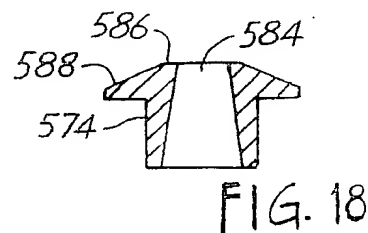
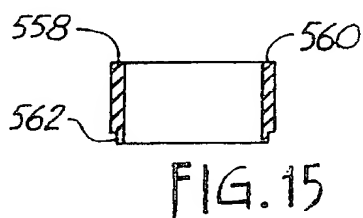
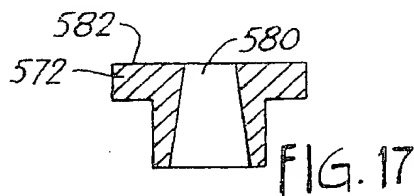
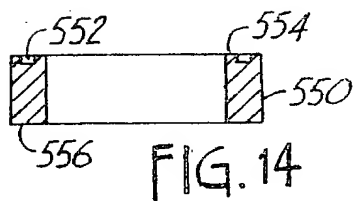
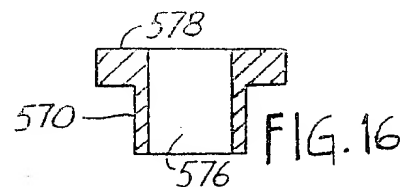
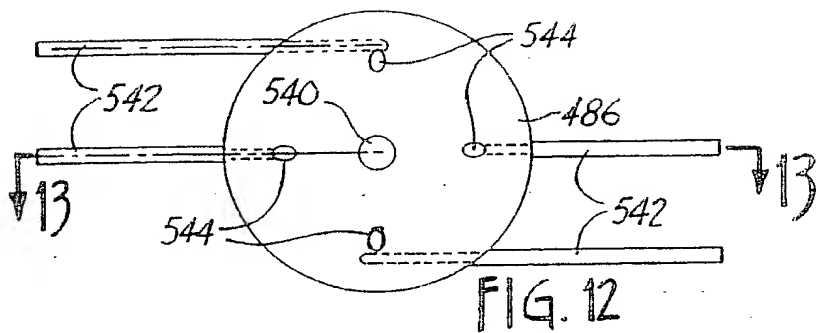
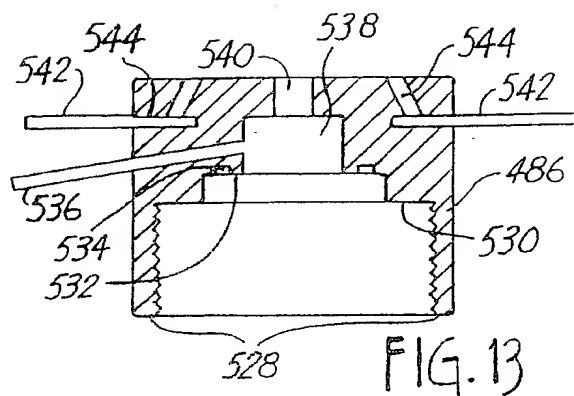
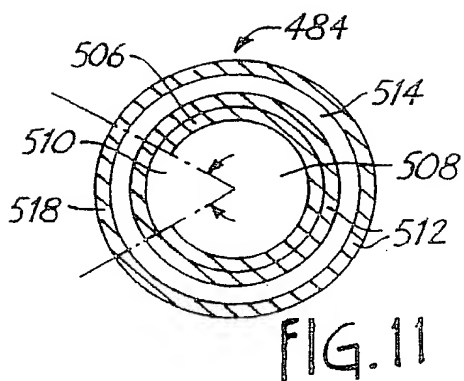
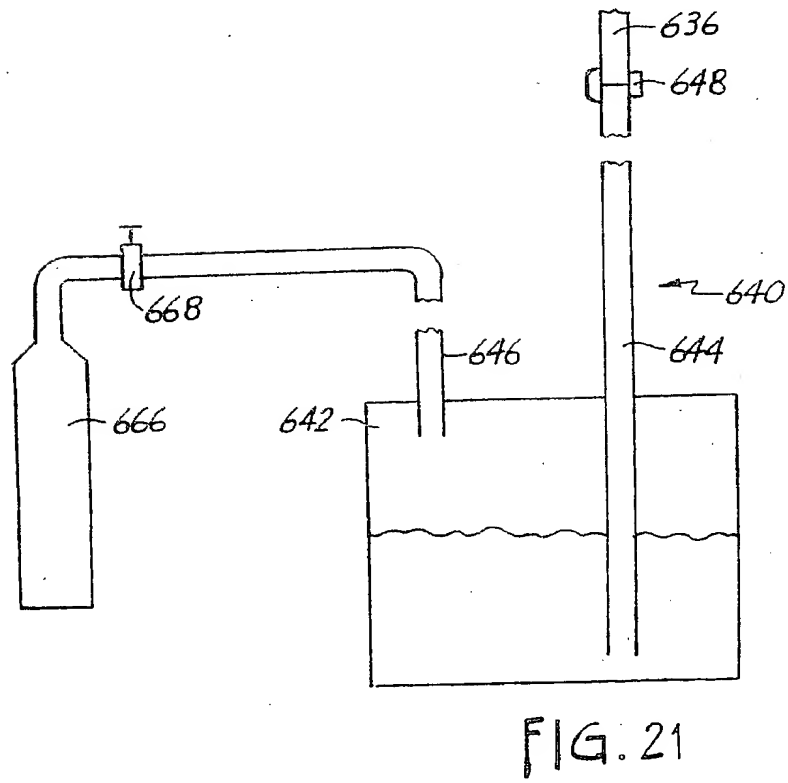
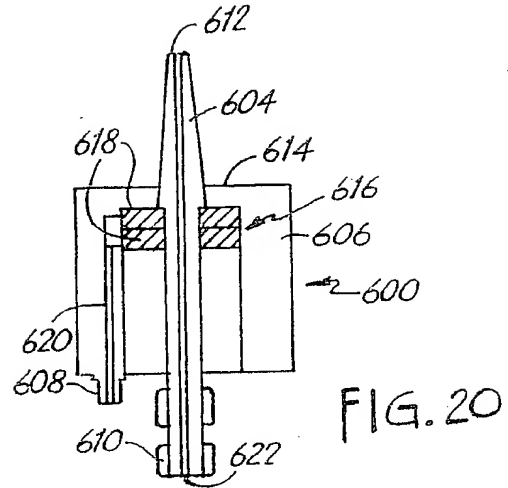
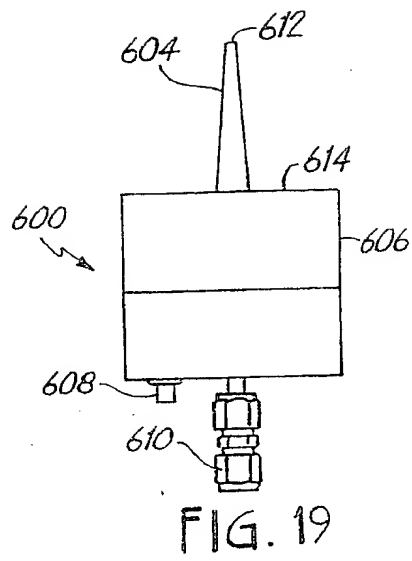
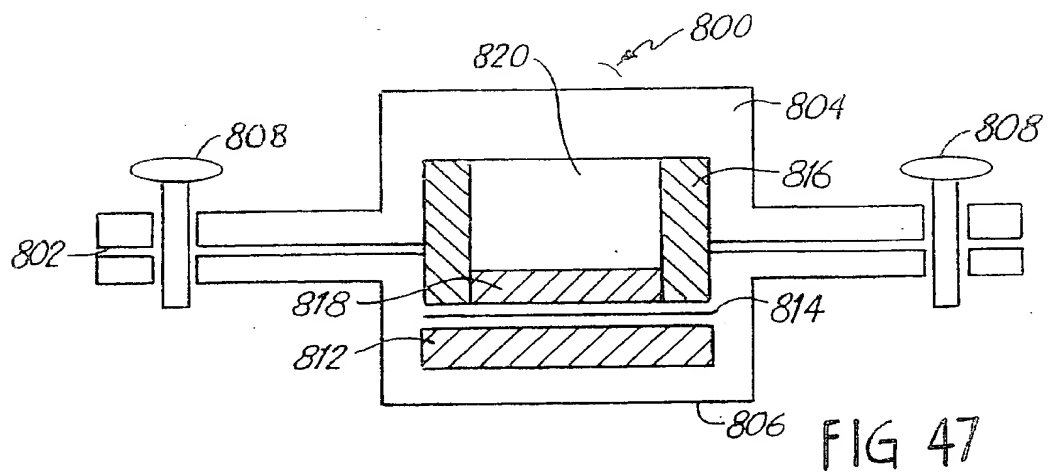
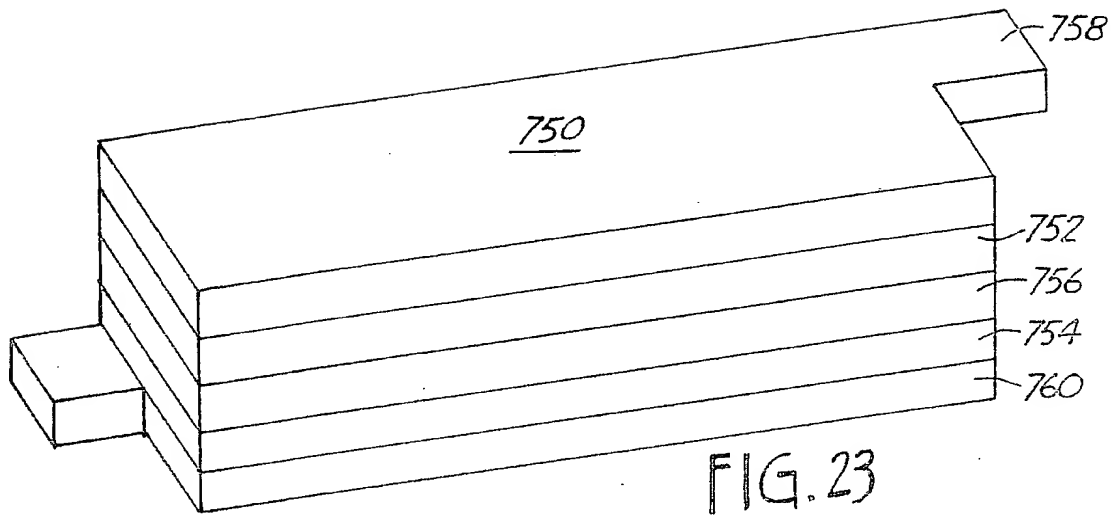


FIG. 8









## MANGANESE OXIDE

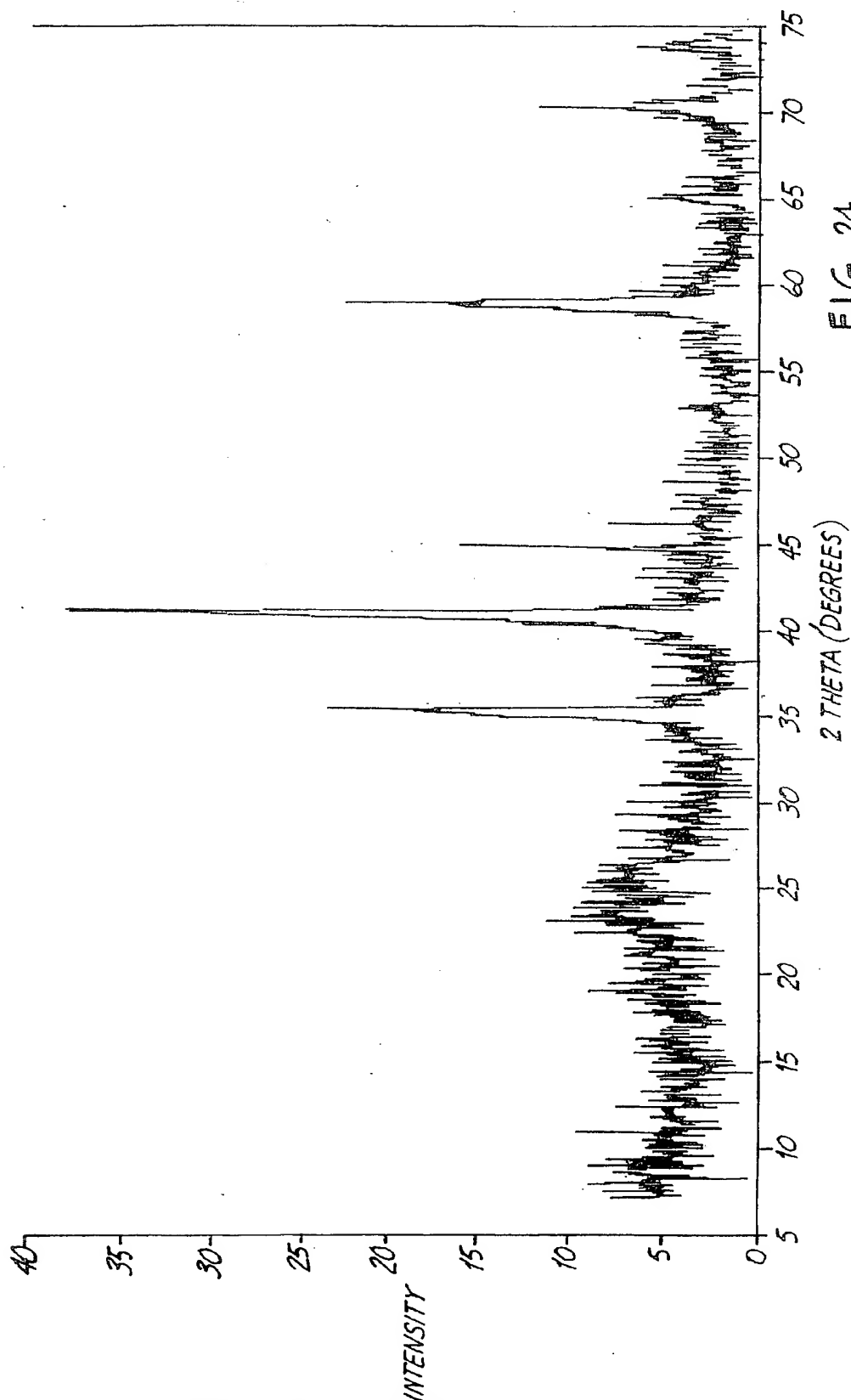


FIG. 24



MANGANESE OXIDE

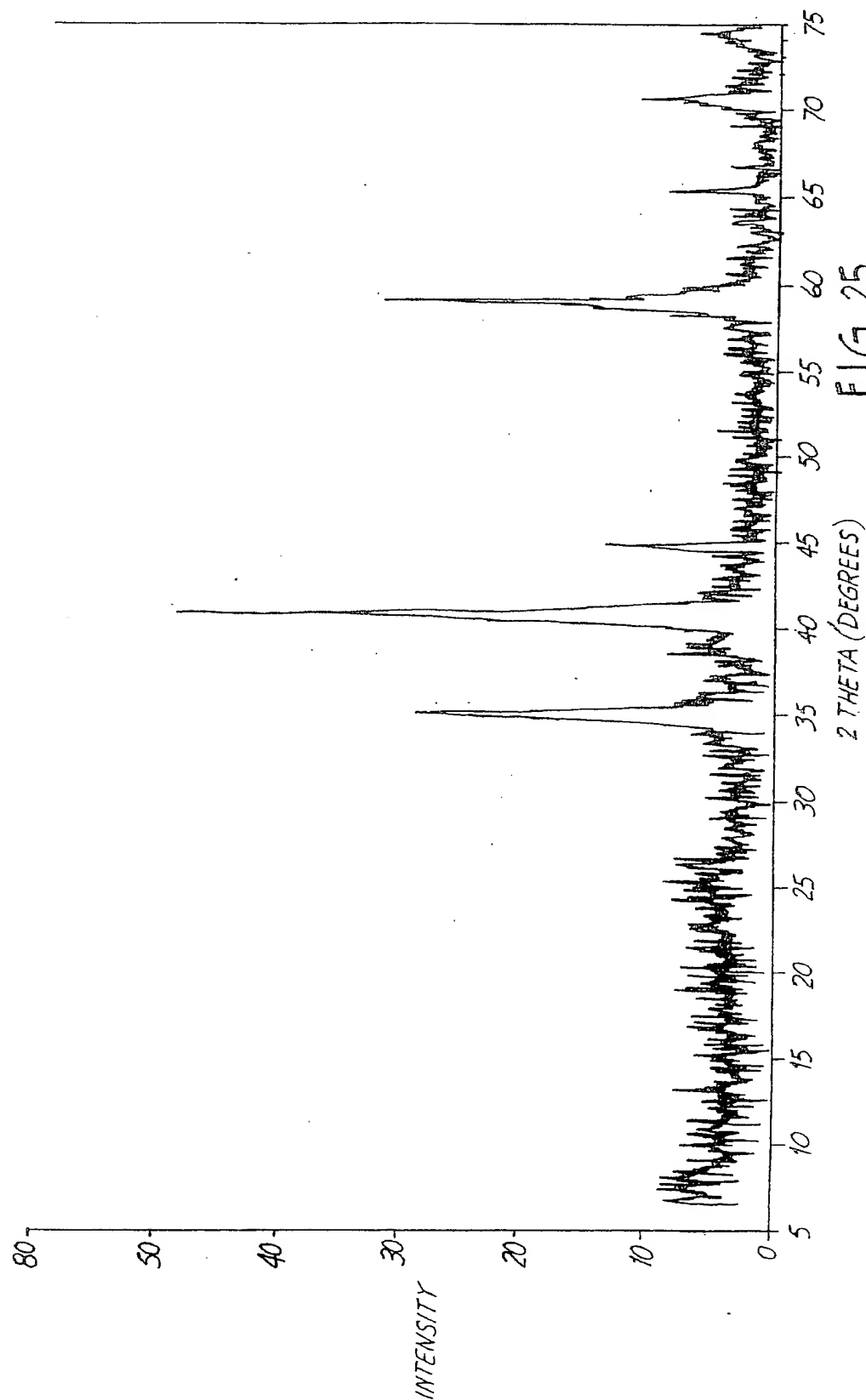
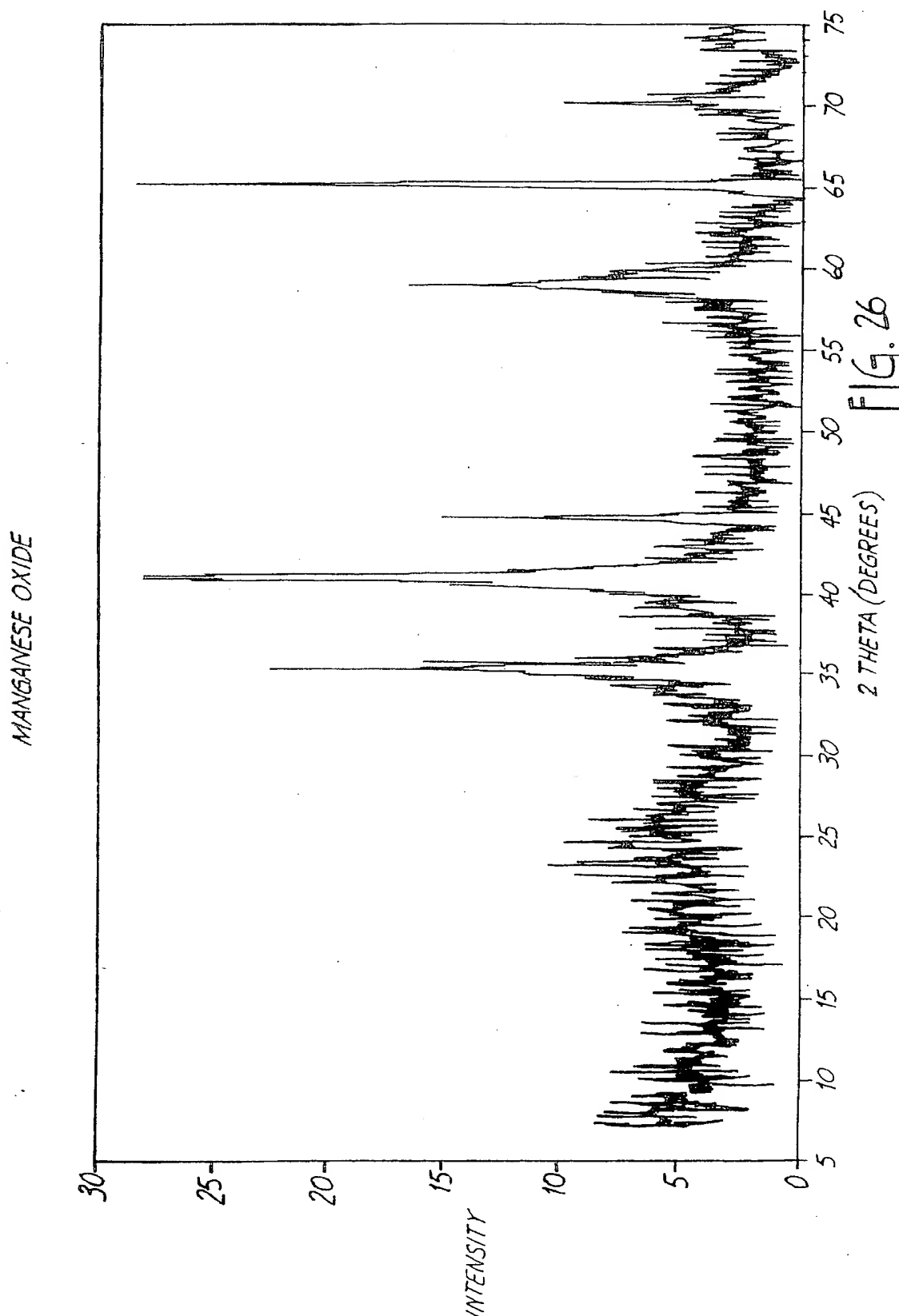


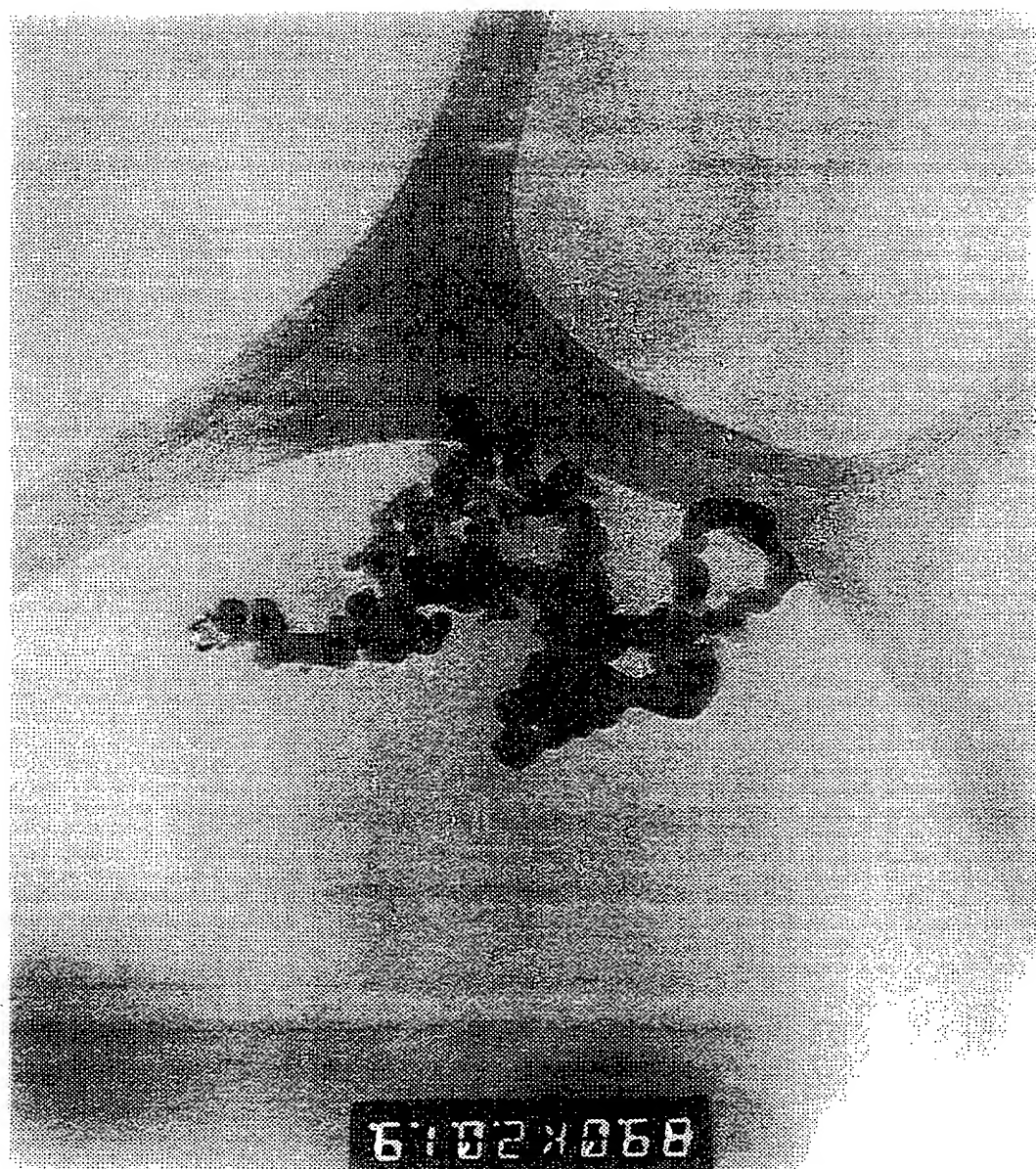
FIG. 25

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FIG. 27



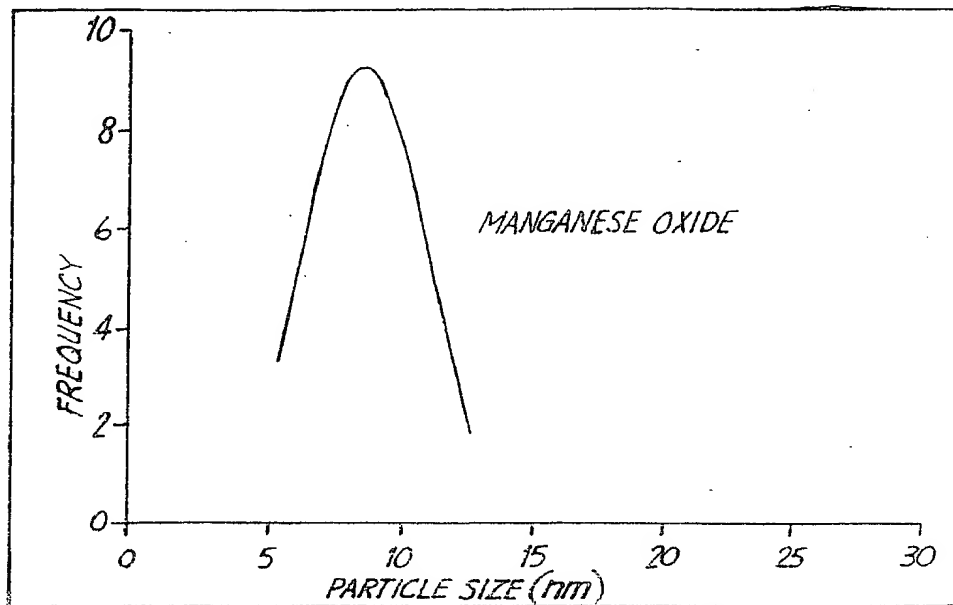


FIG. 28

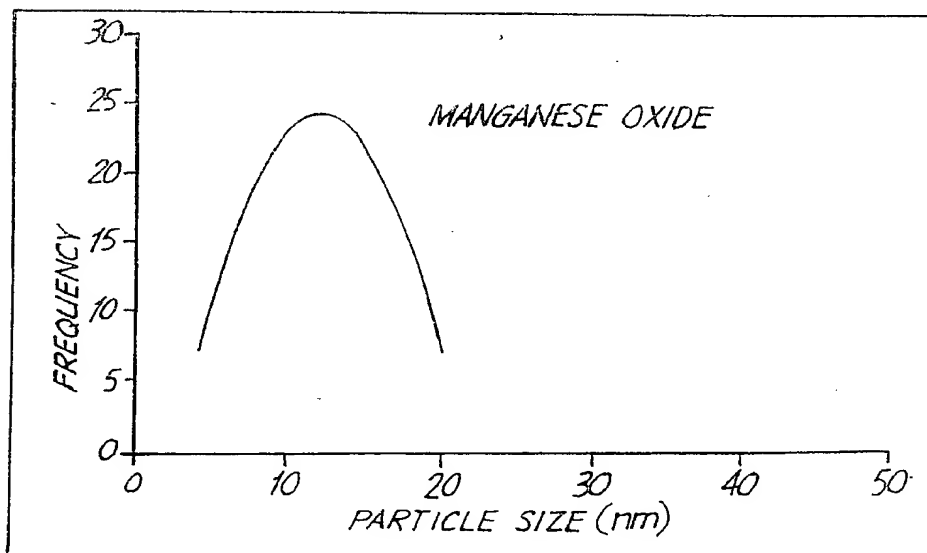


FIG. 31

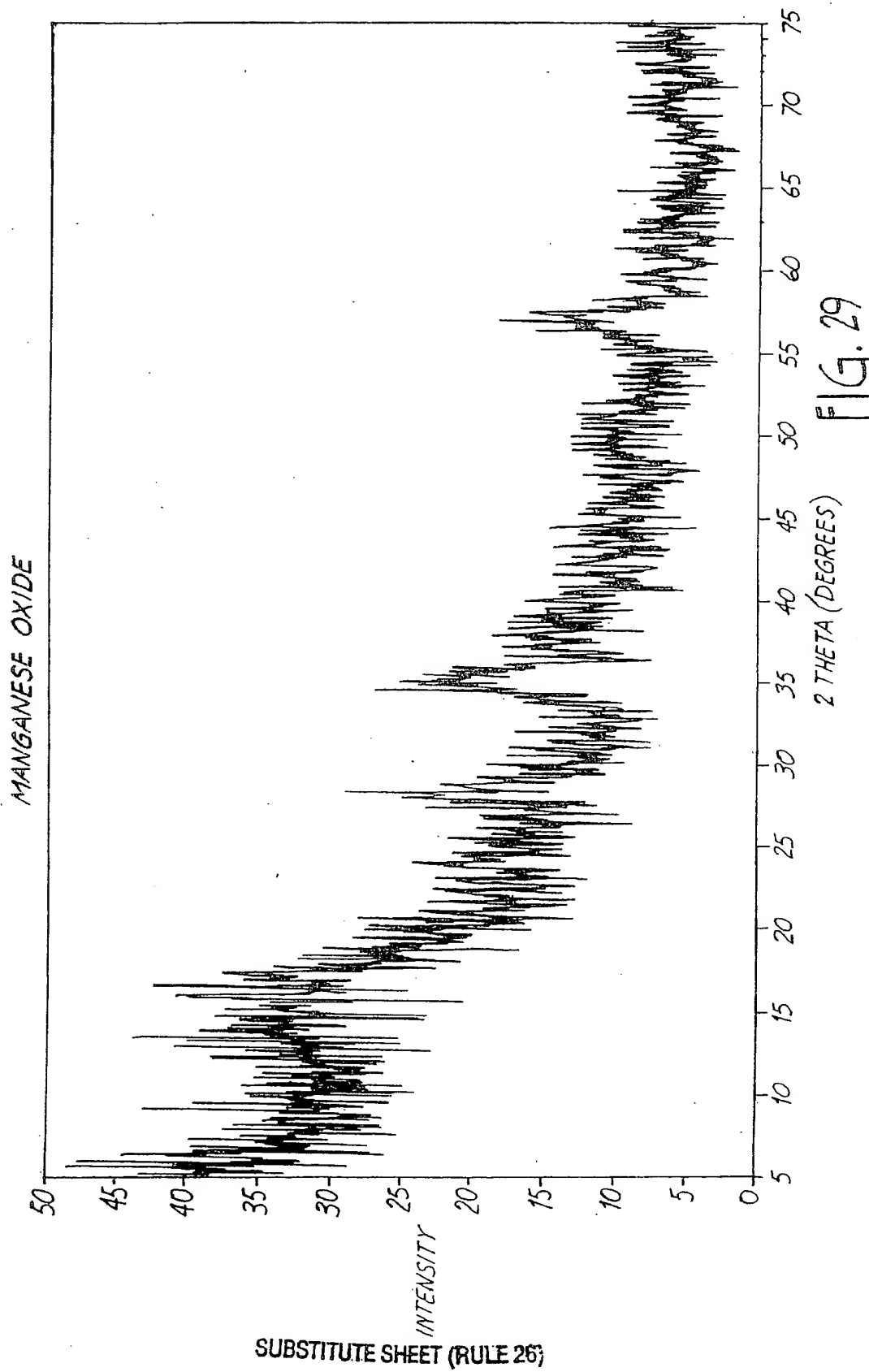
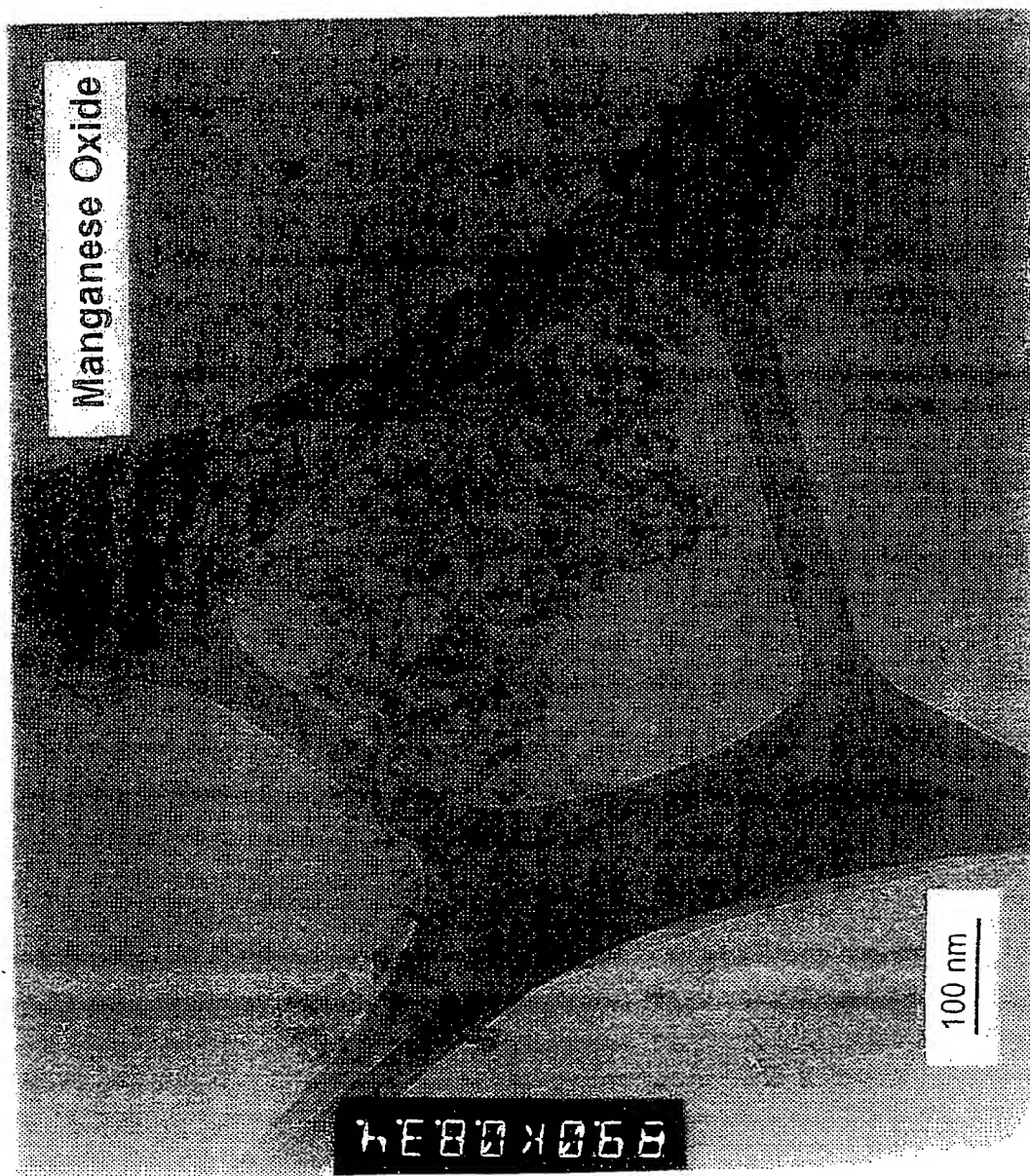
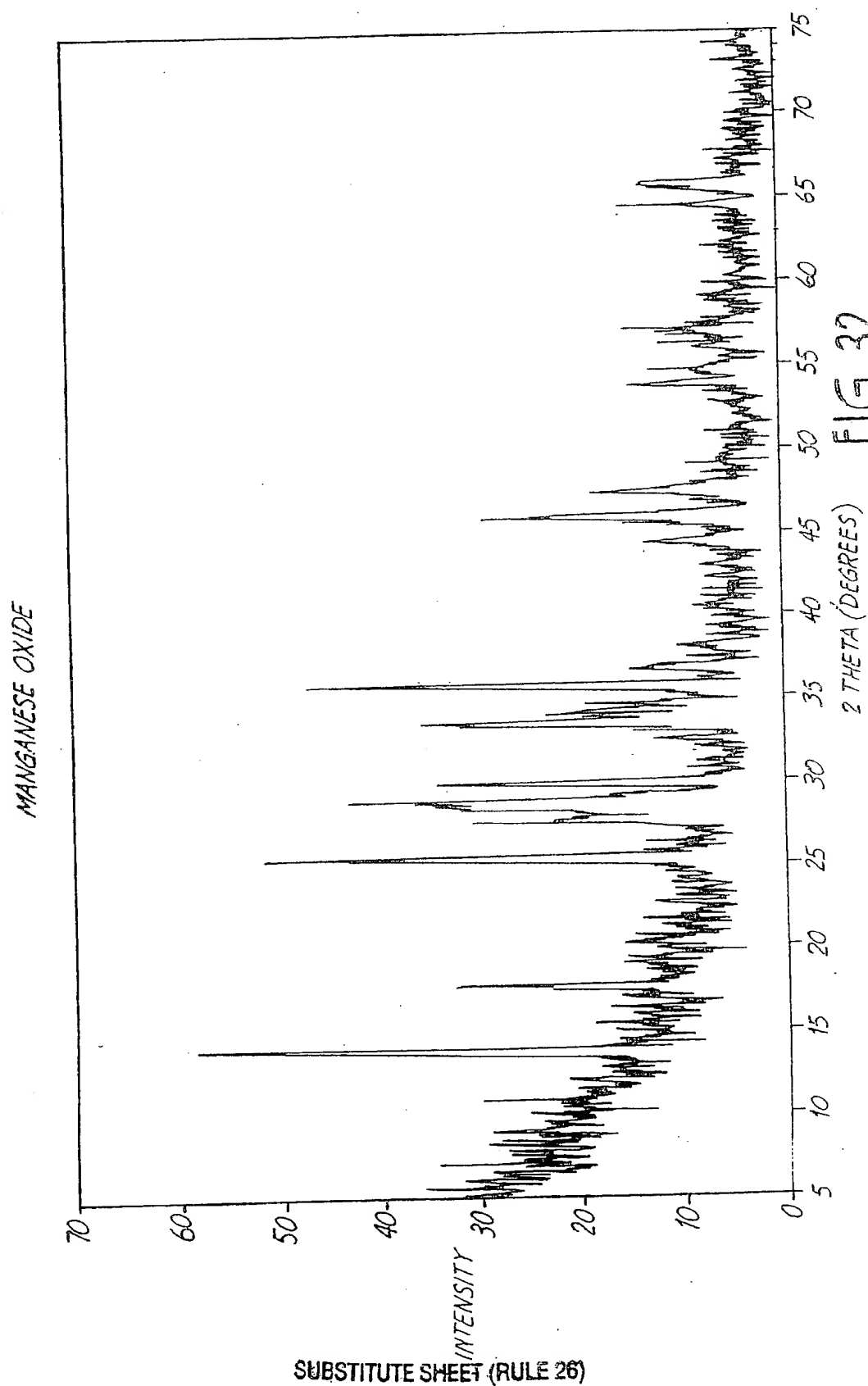
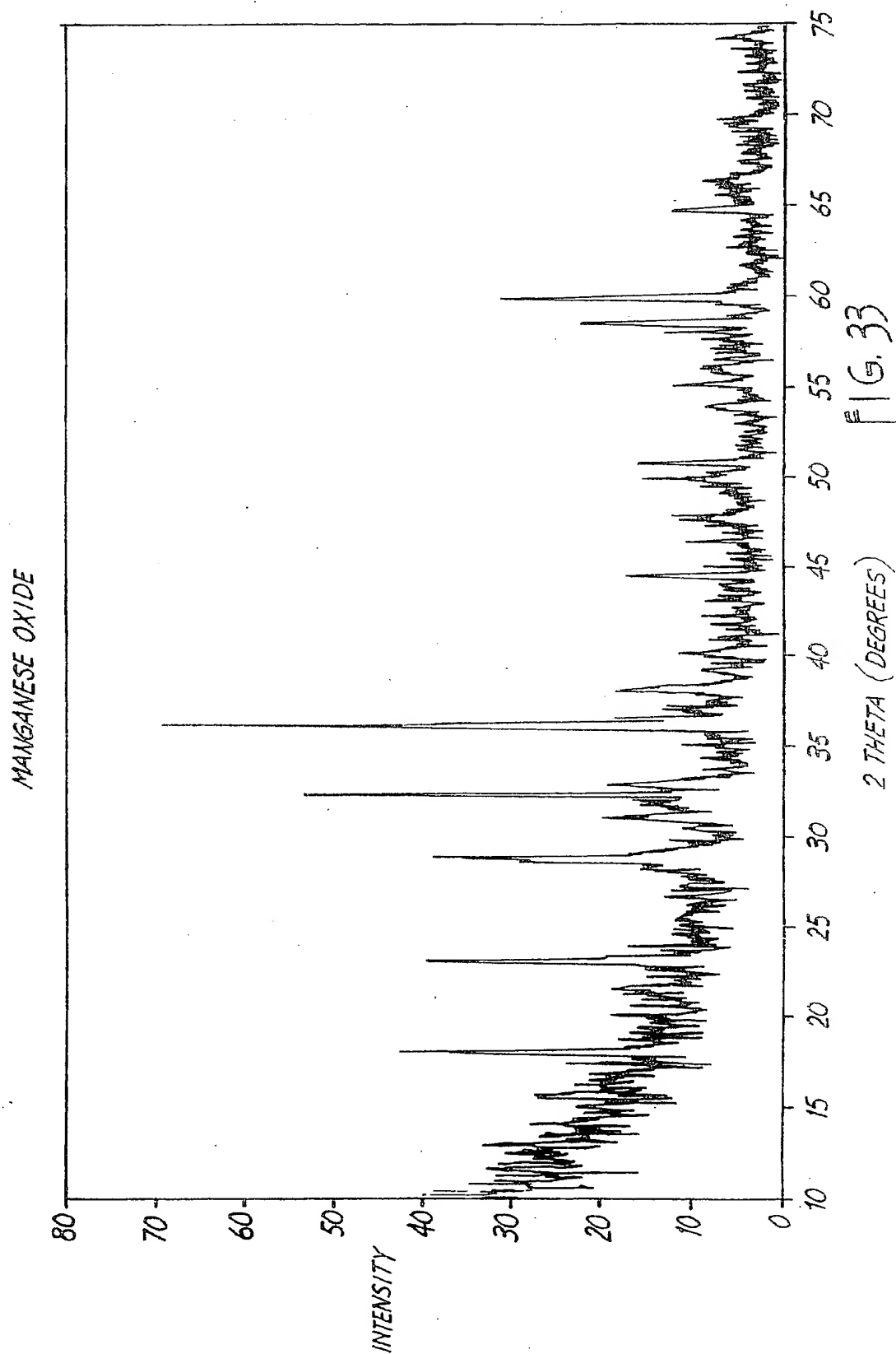


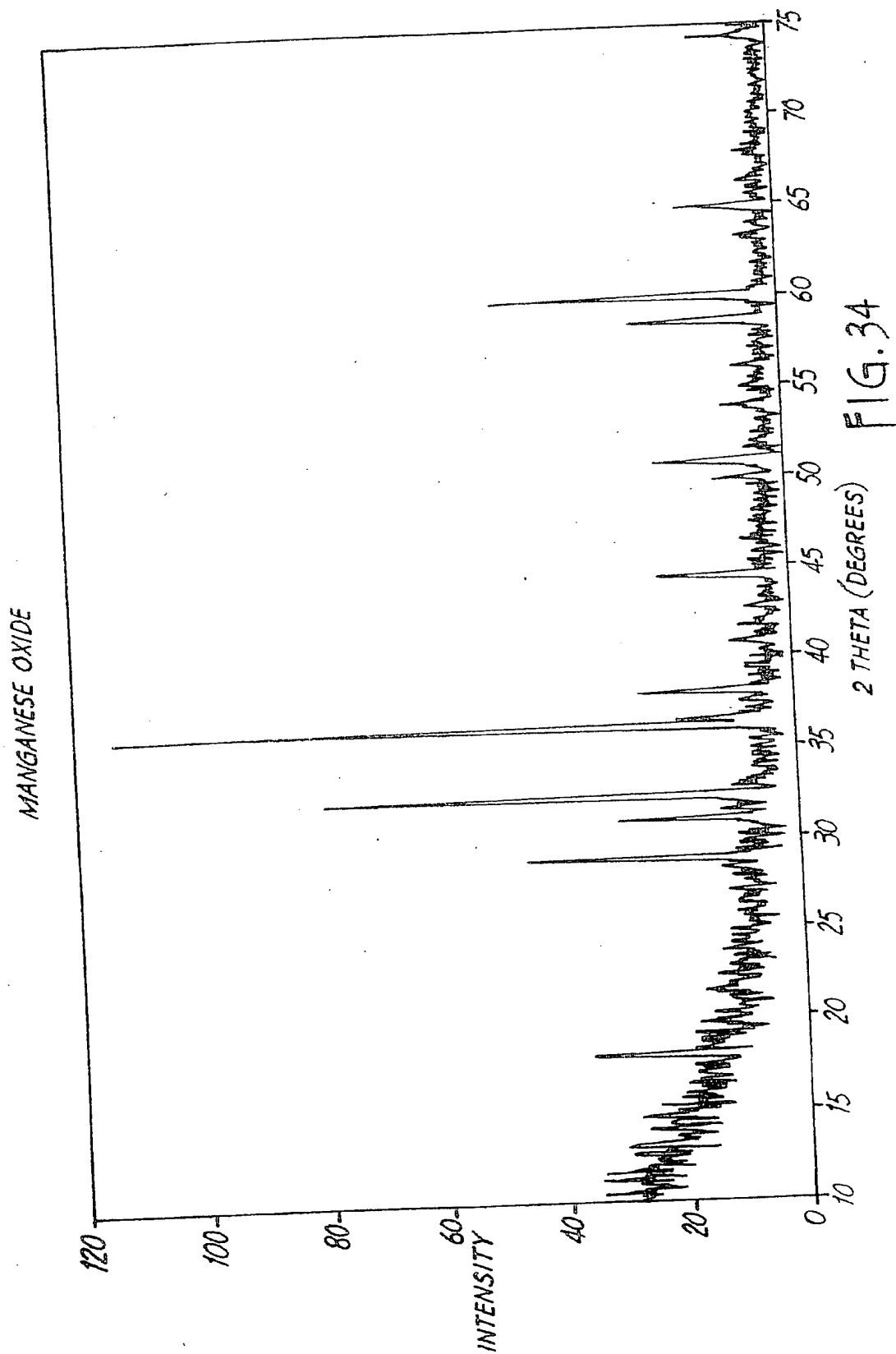
FIG. 30

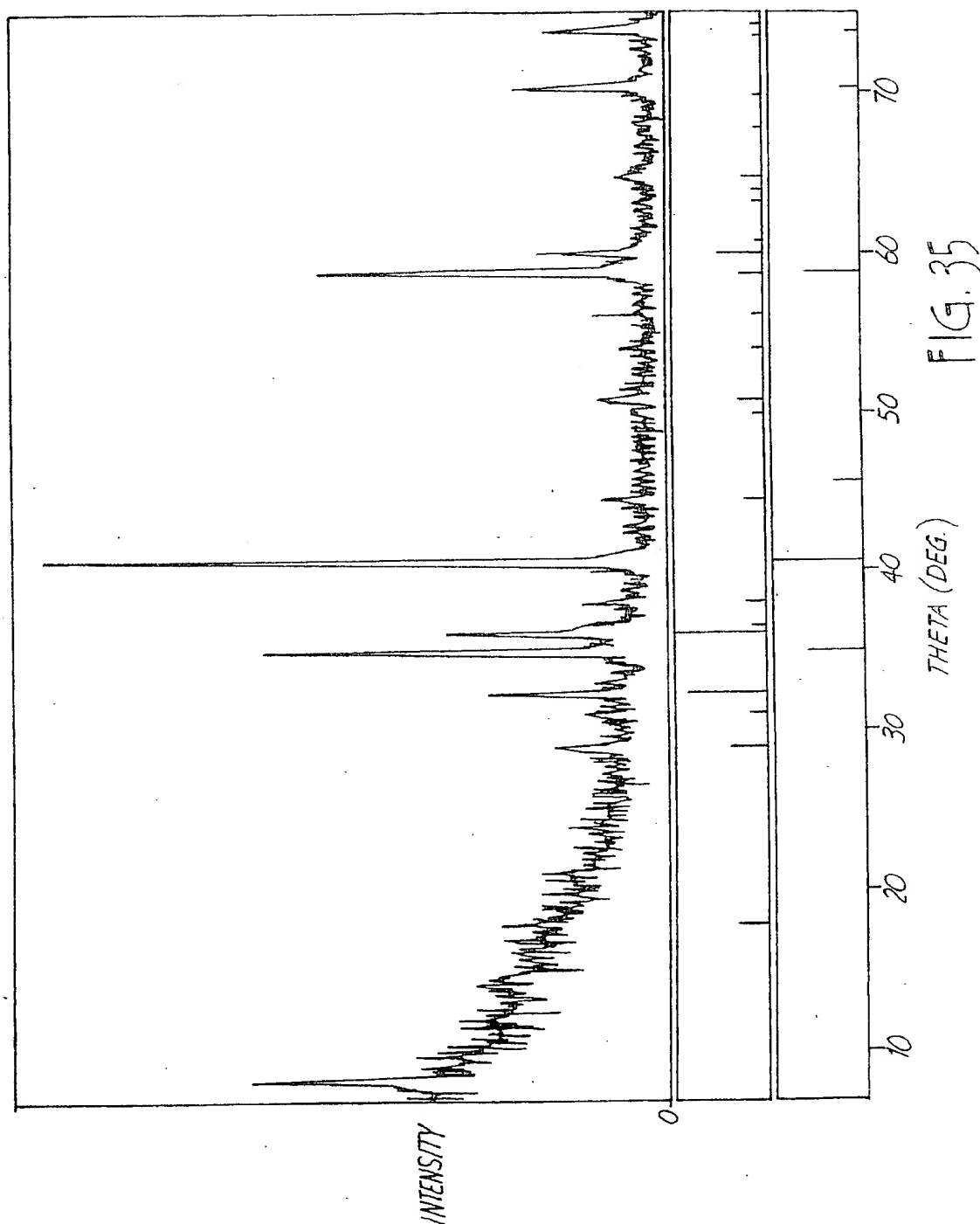












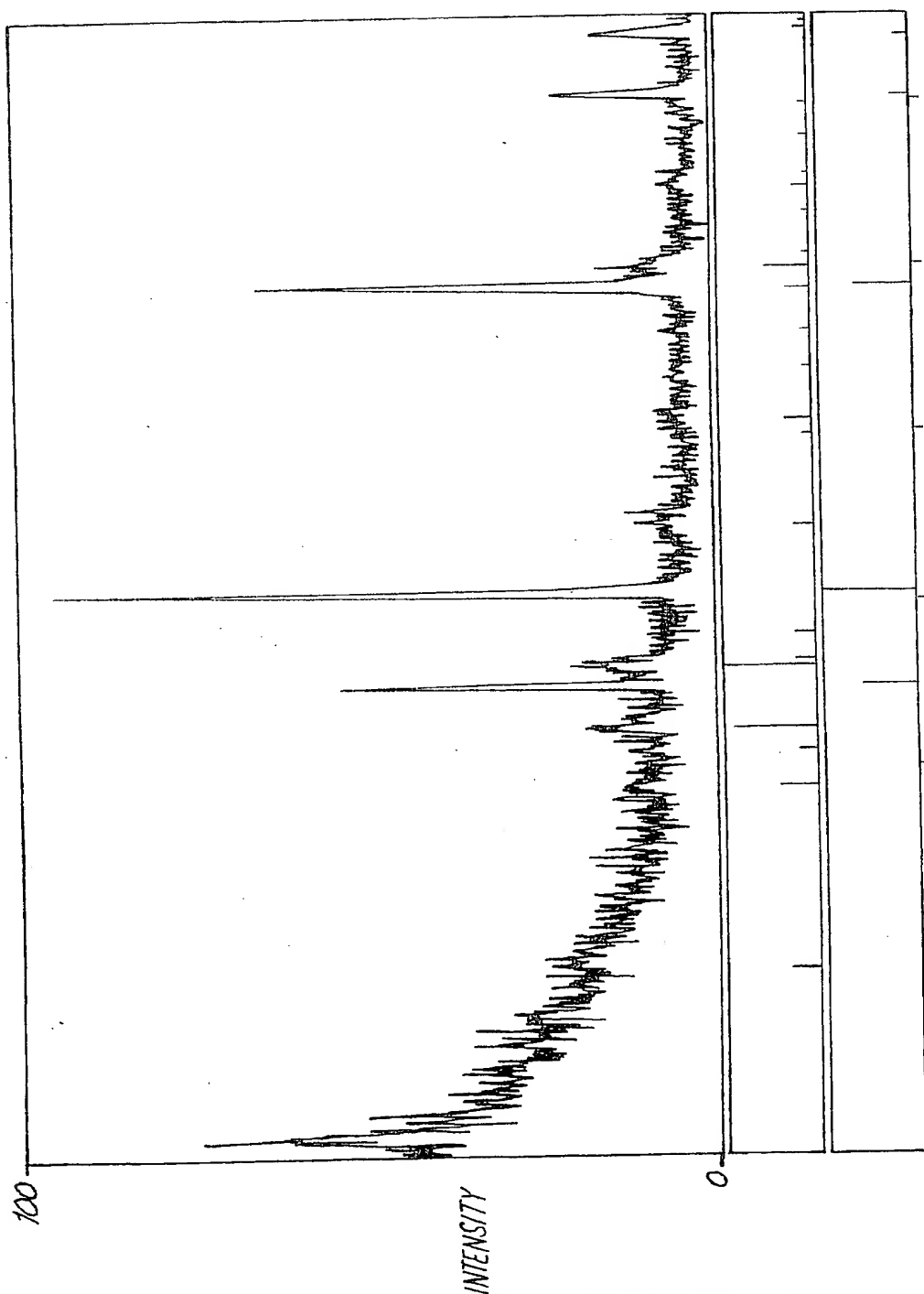
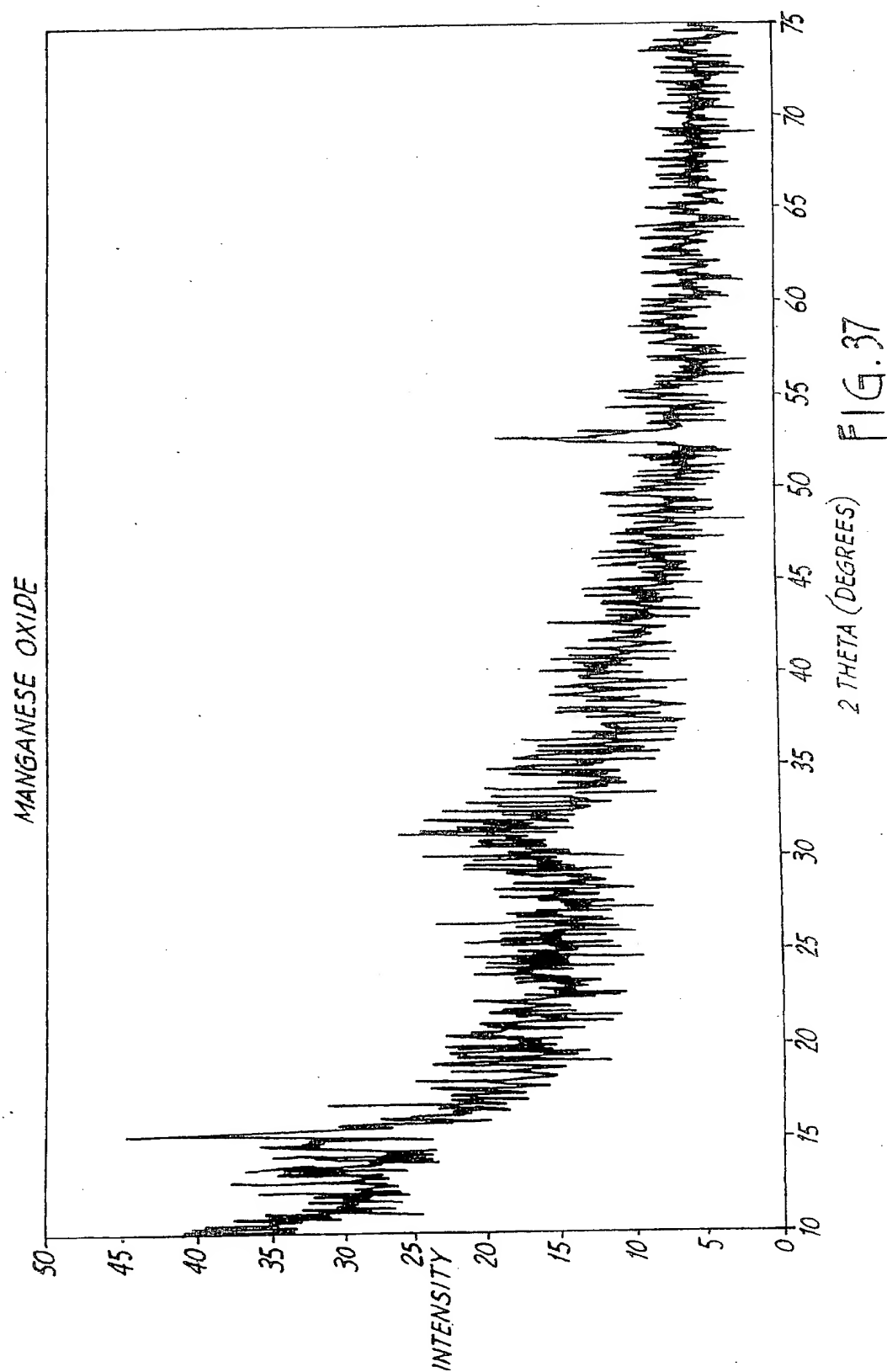
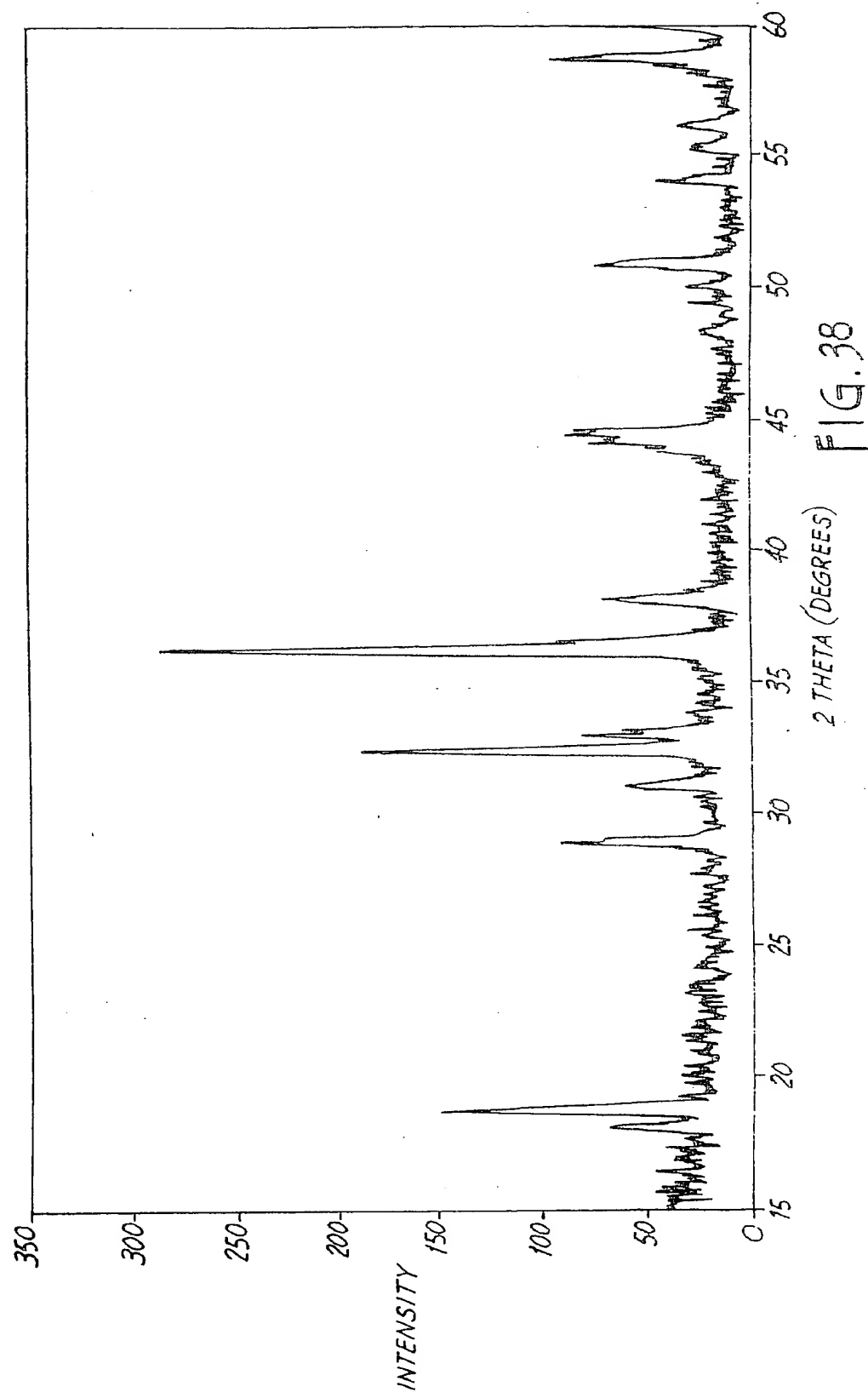


FIG. 36





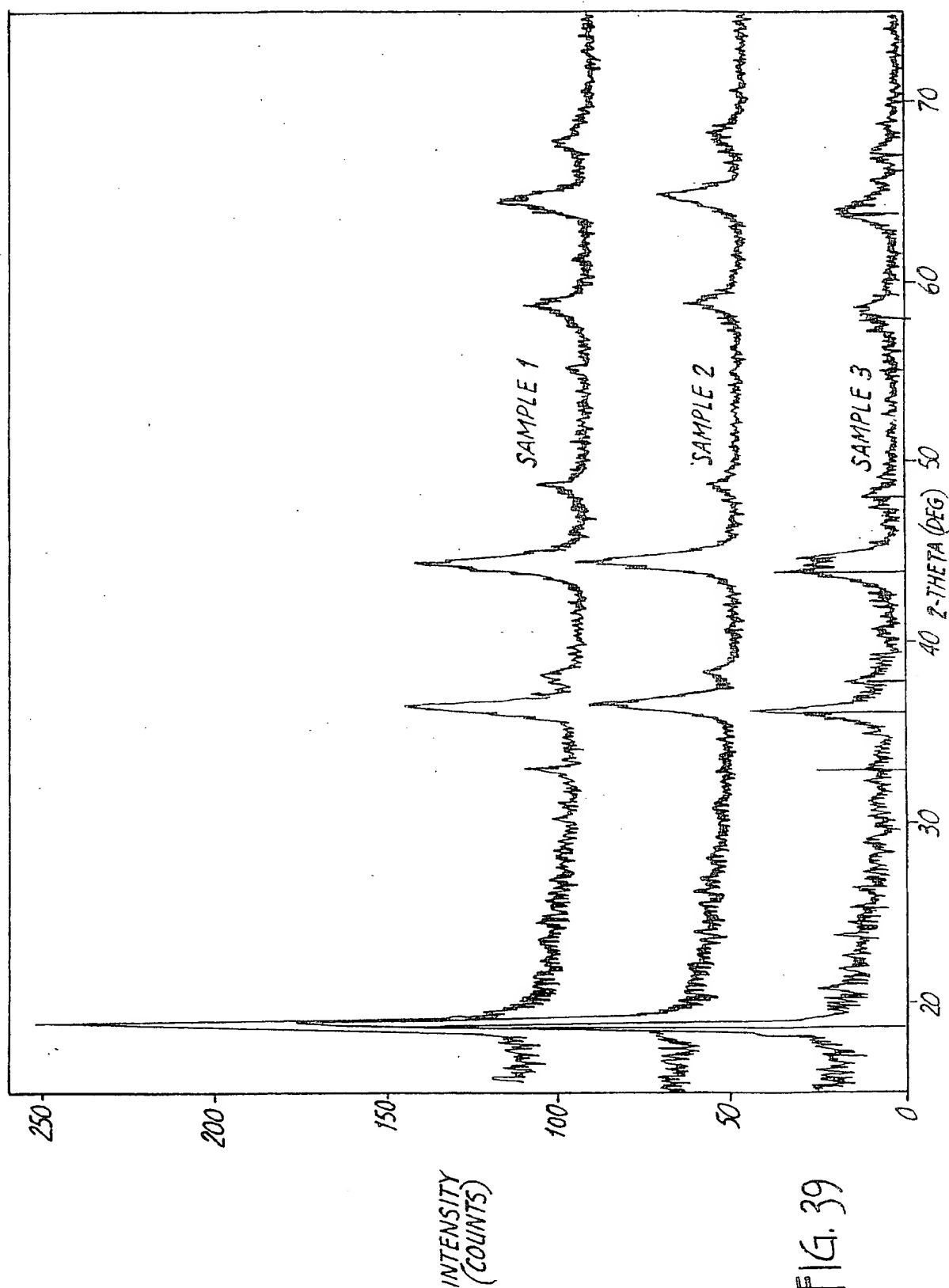
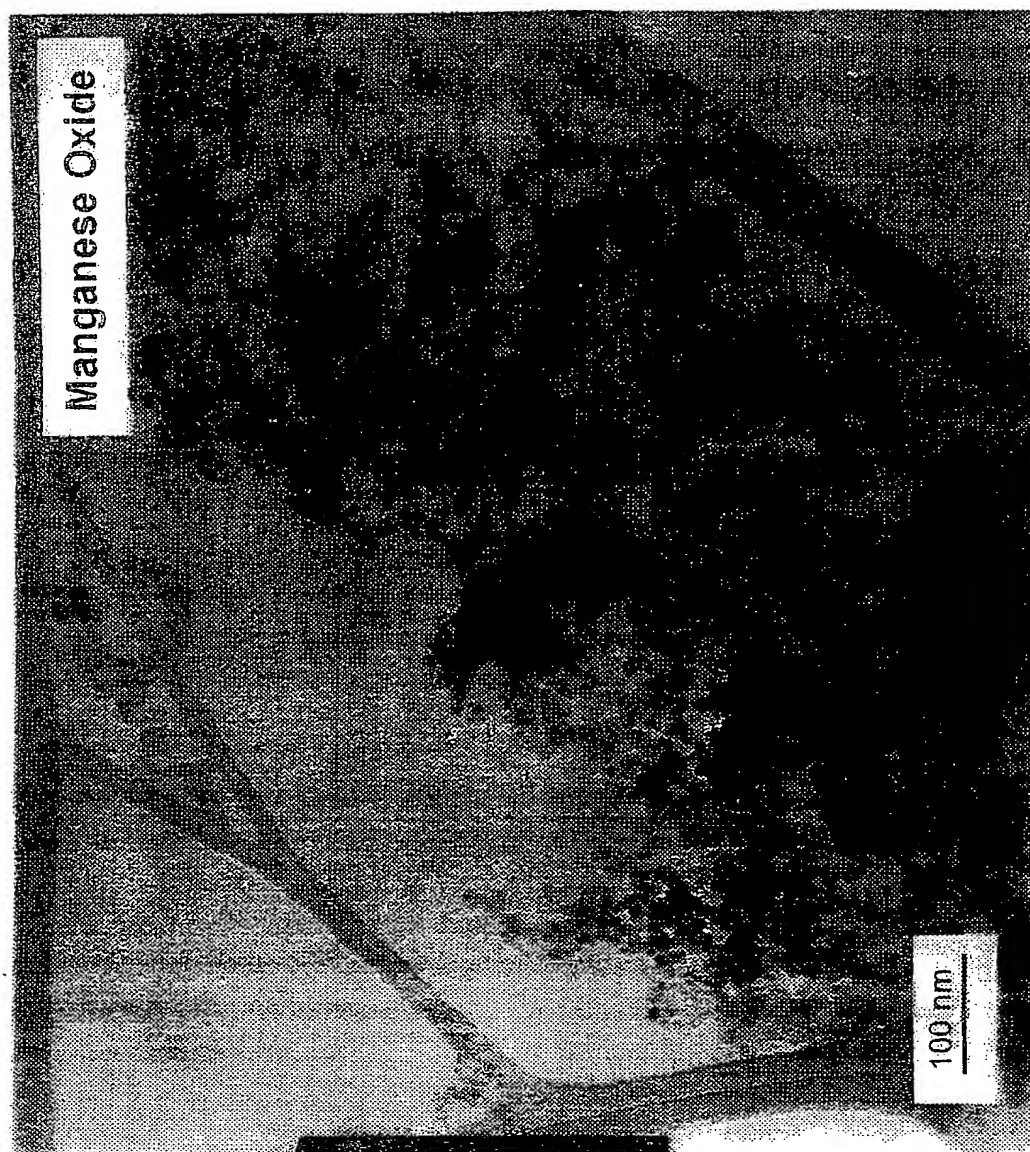


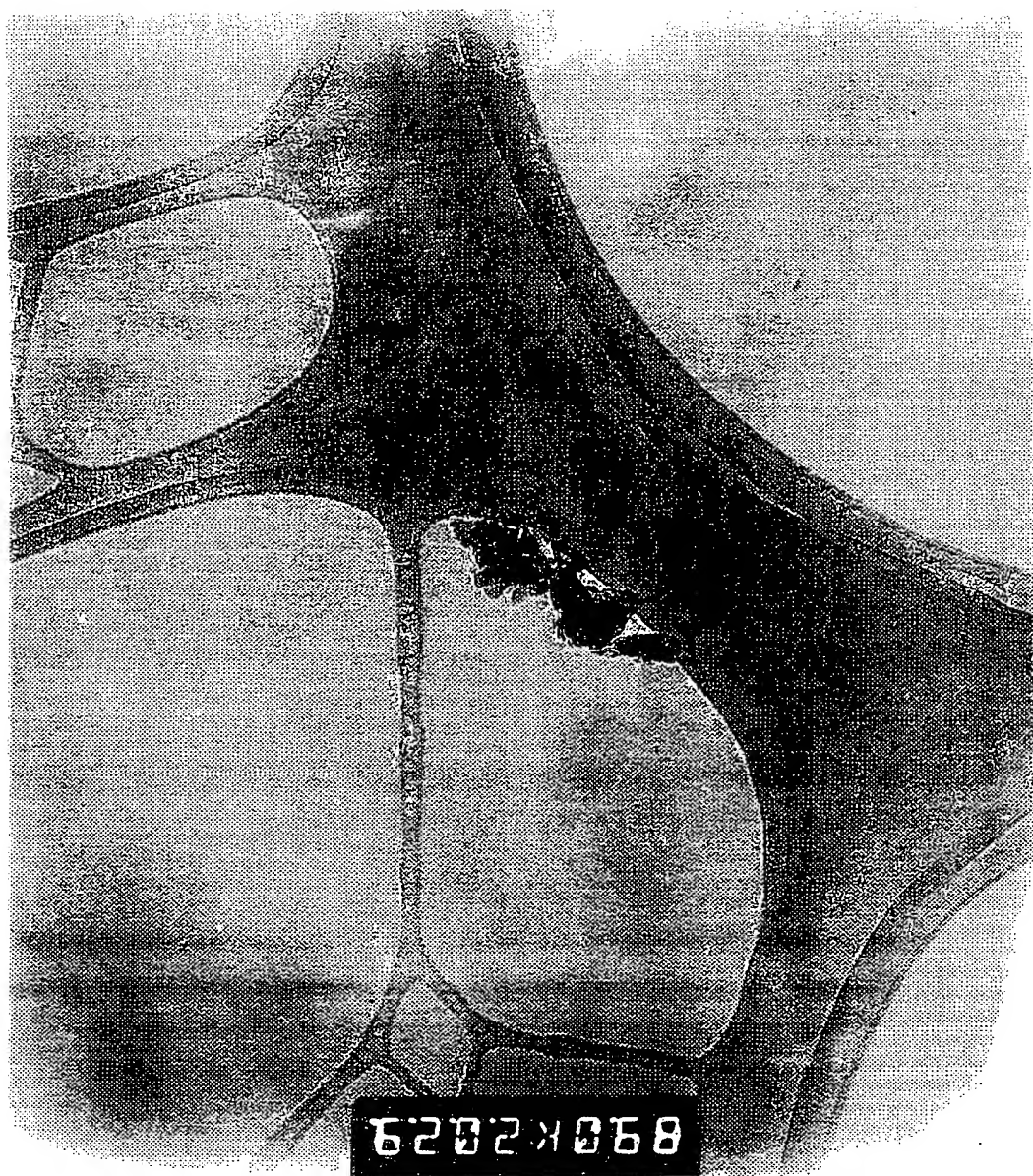
FIG. 39

FIG. 40



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FIG. 41



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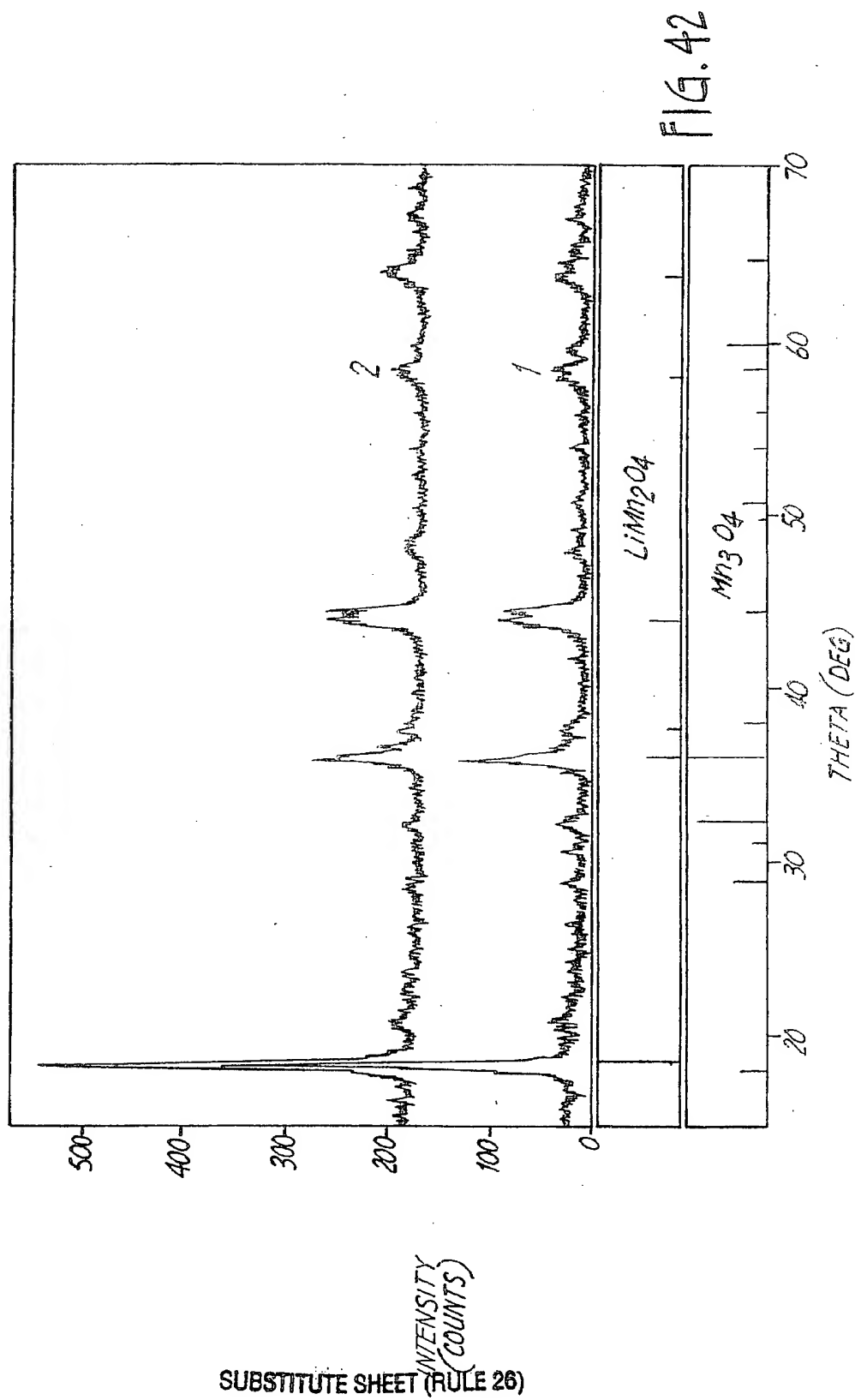
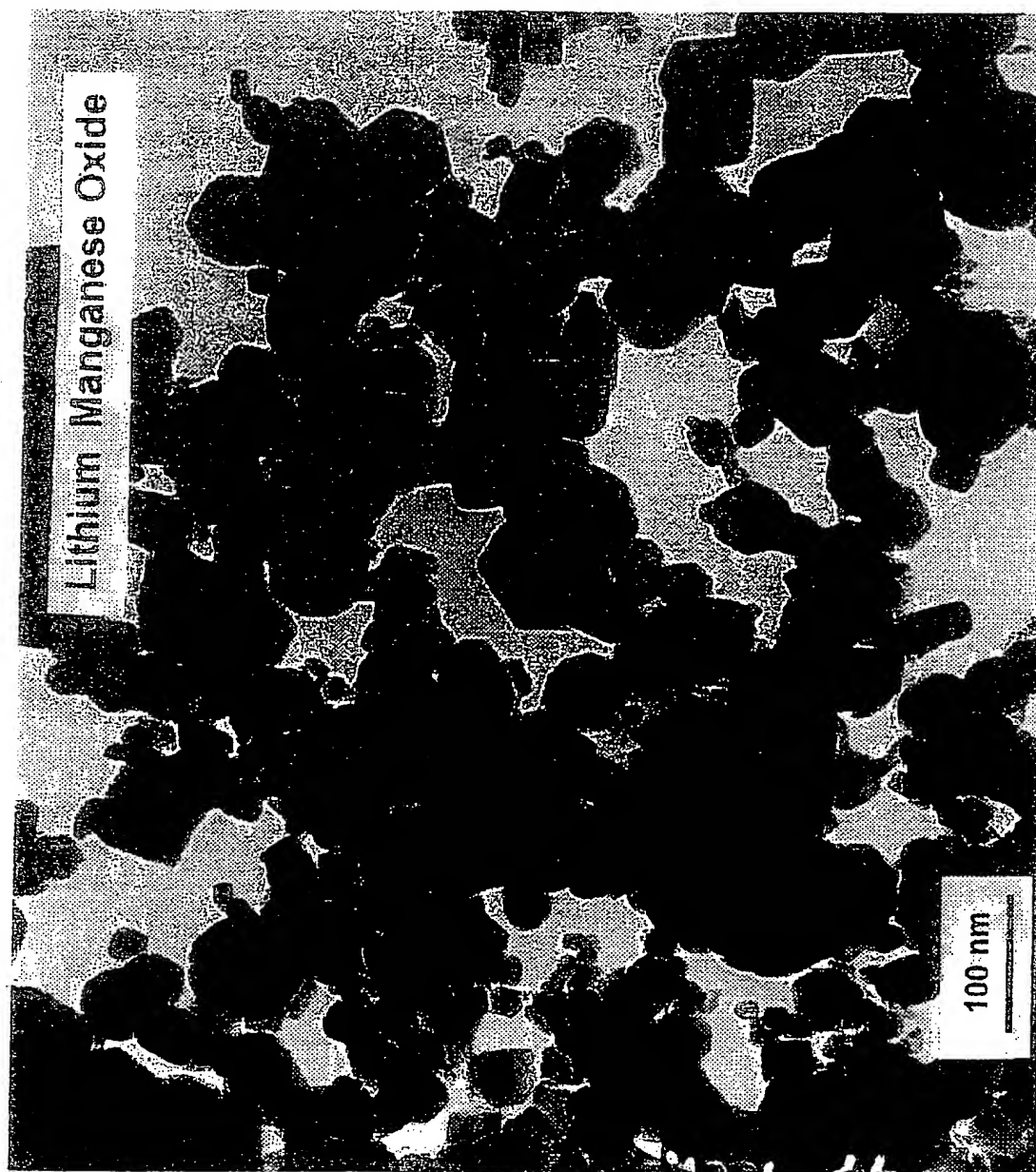


Fig. 43



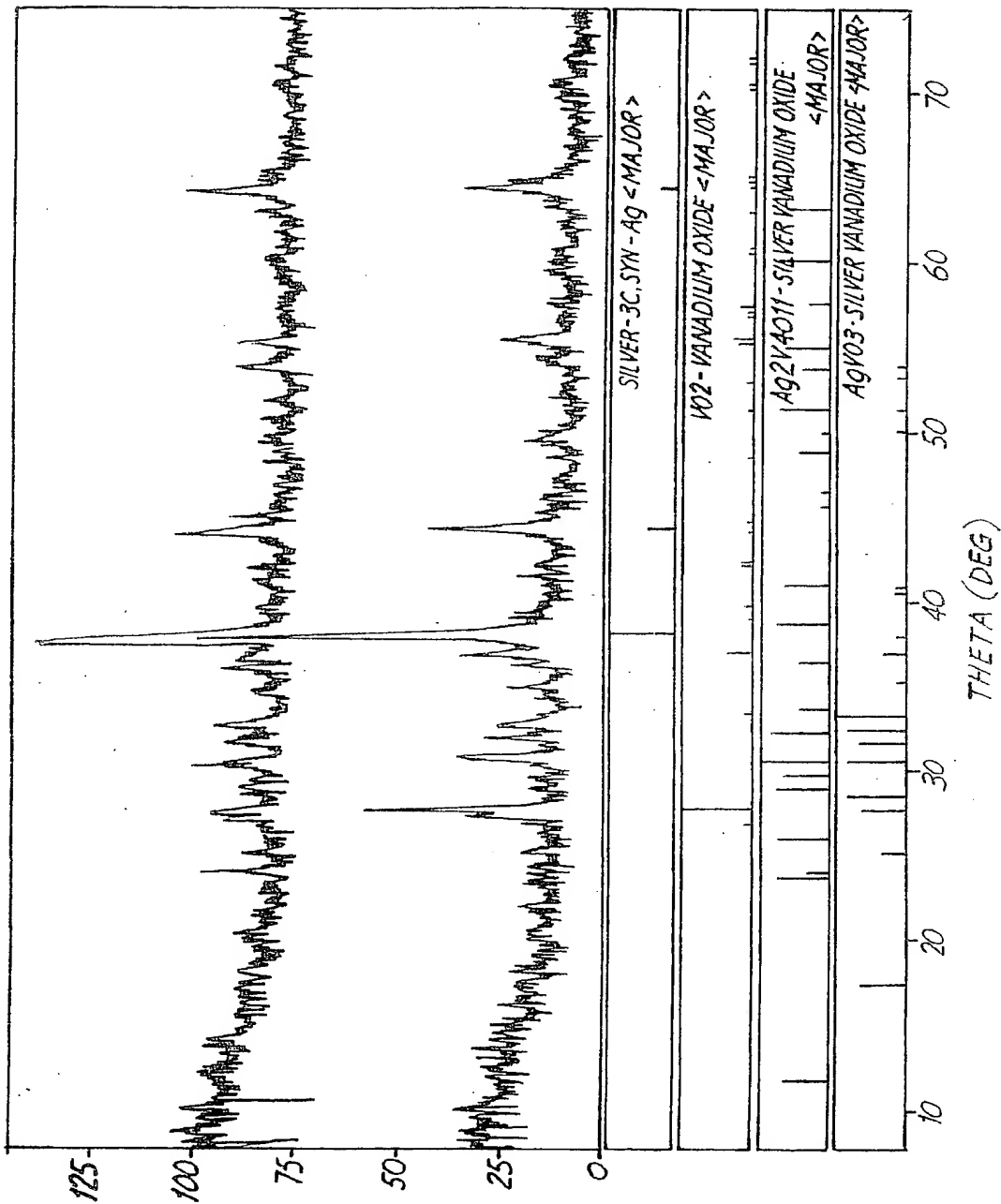
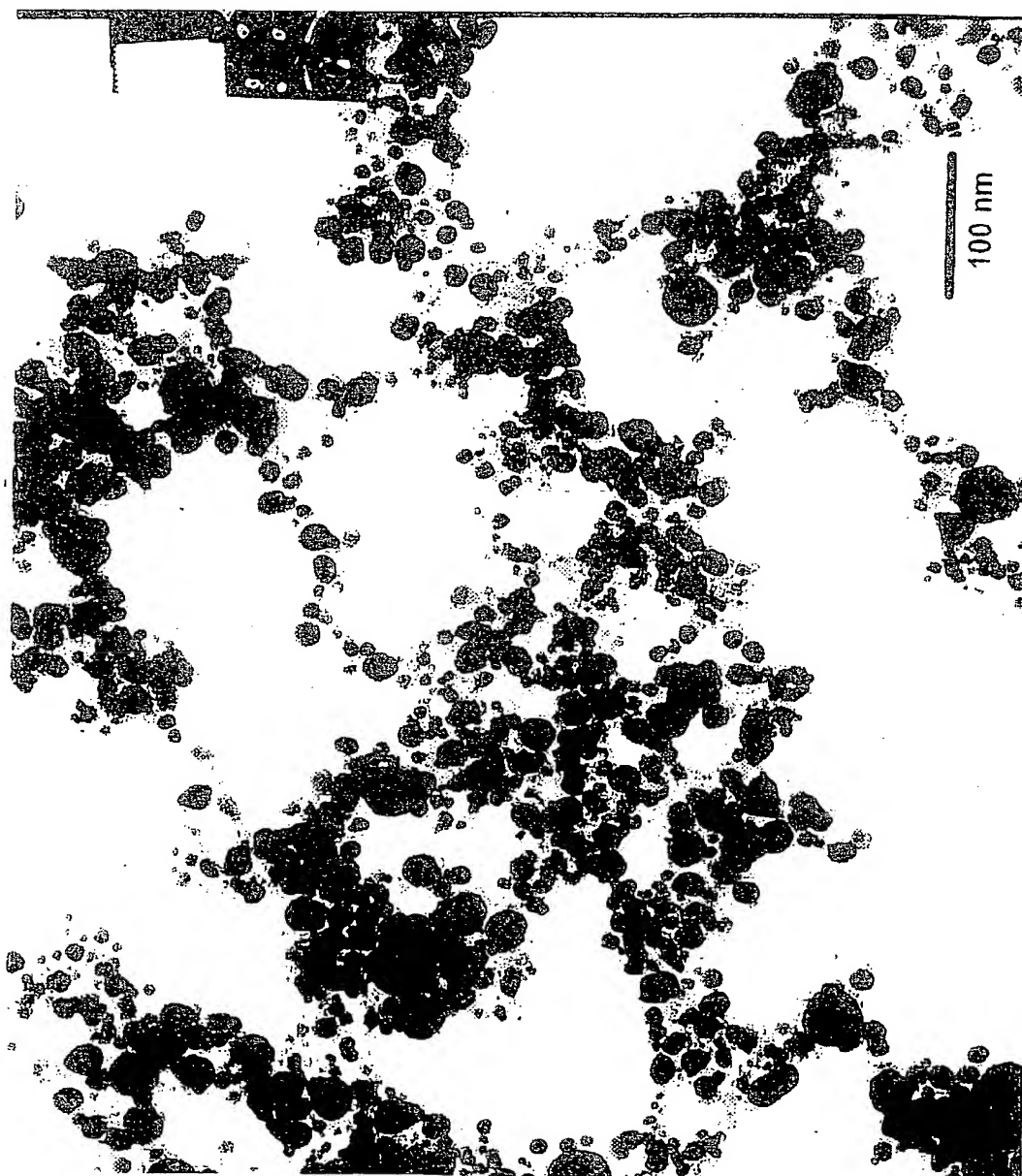


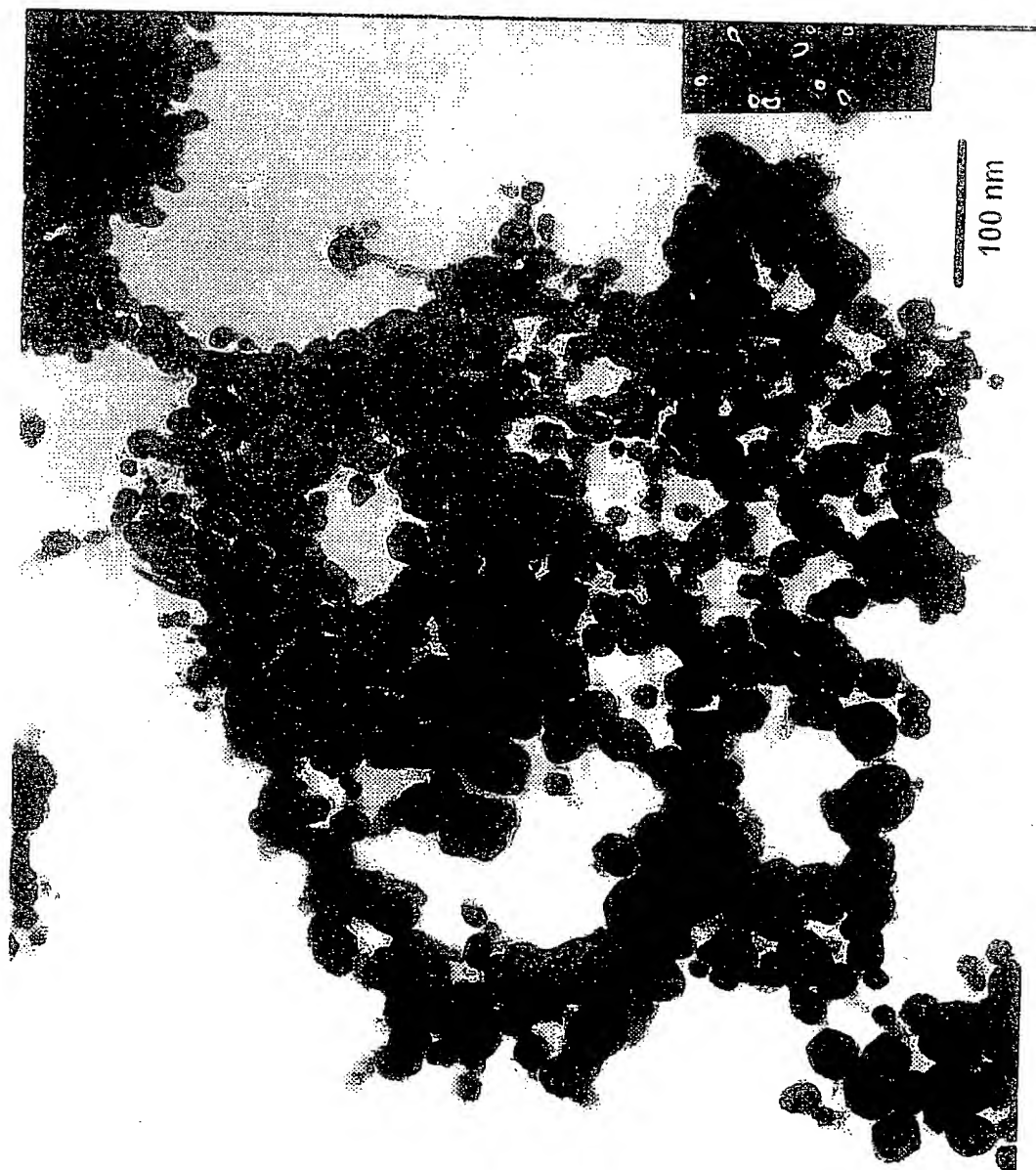
FIG. 44

FIG. 45A



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FIG. 45B



SUBSTITUTE SHEET (RULE 26)

## LITHIUM MANGANESE OXIDE

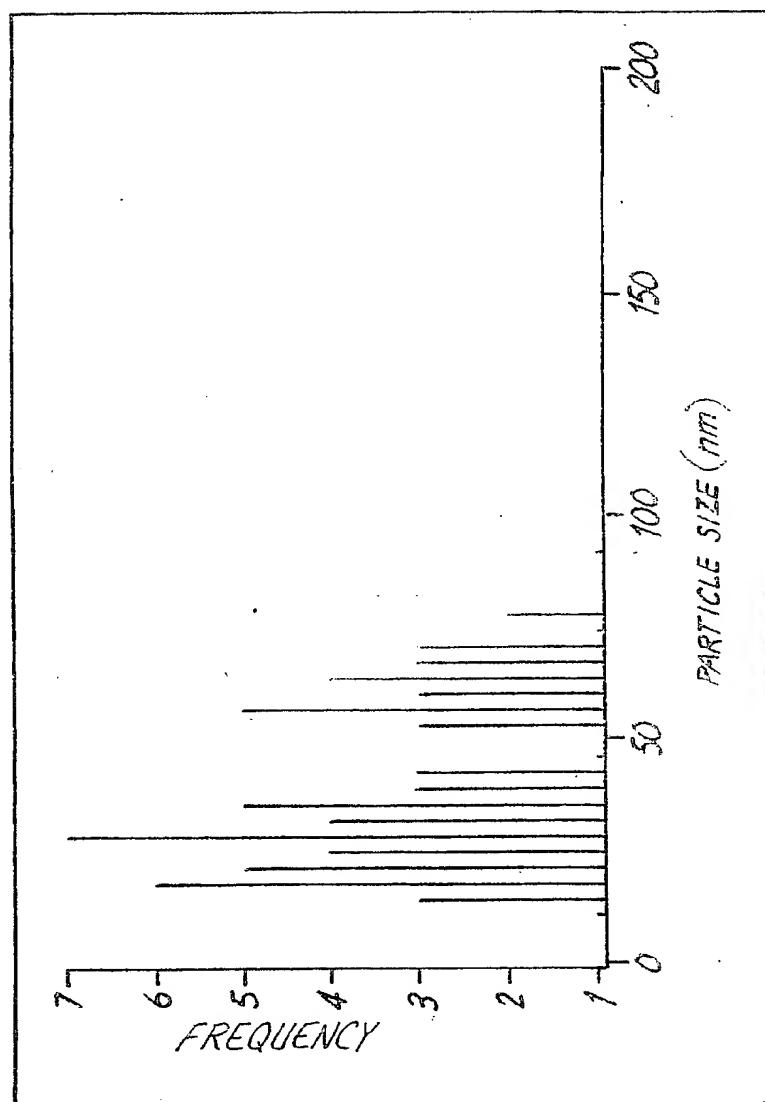


FIG. 46

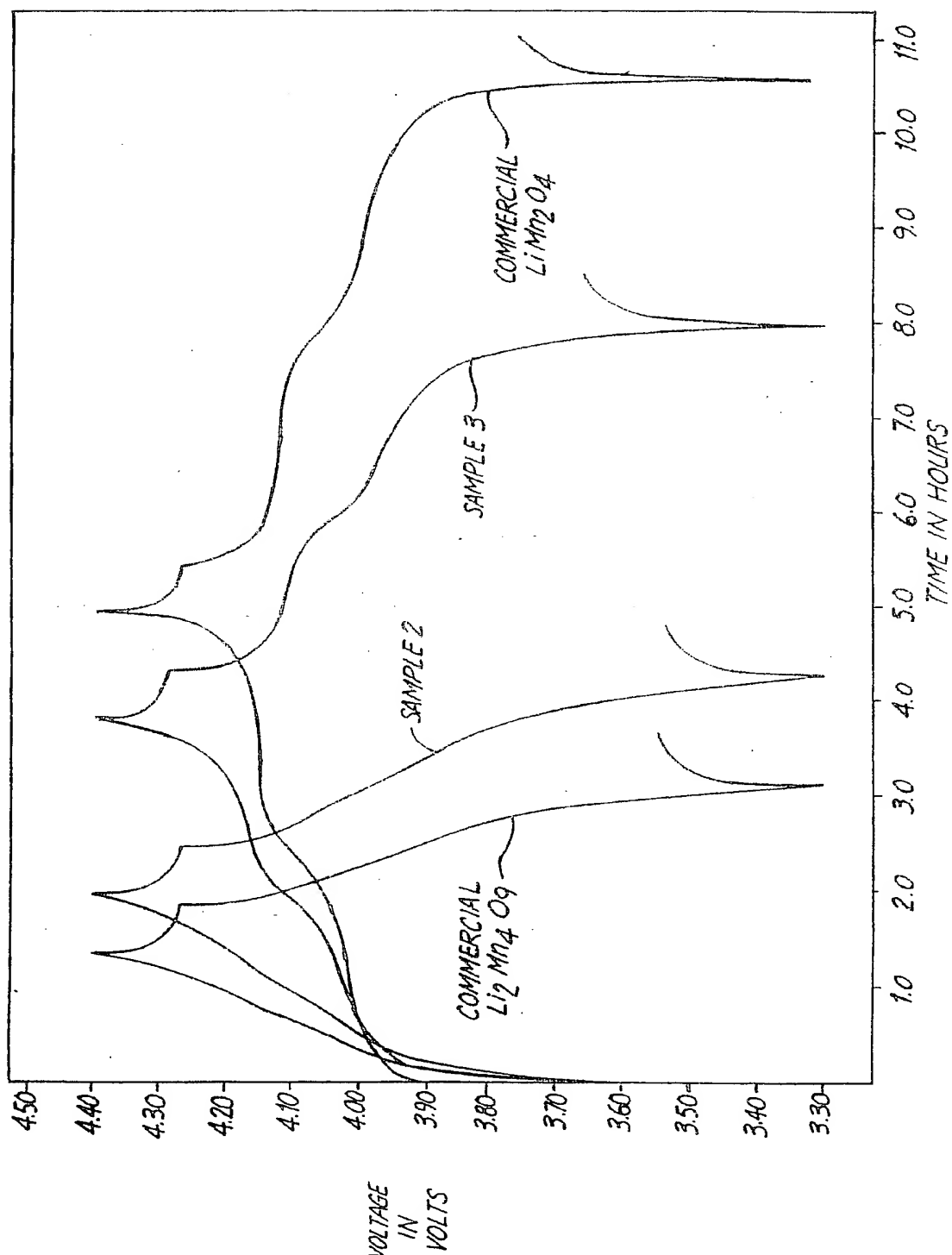


FIG. 48

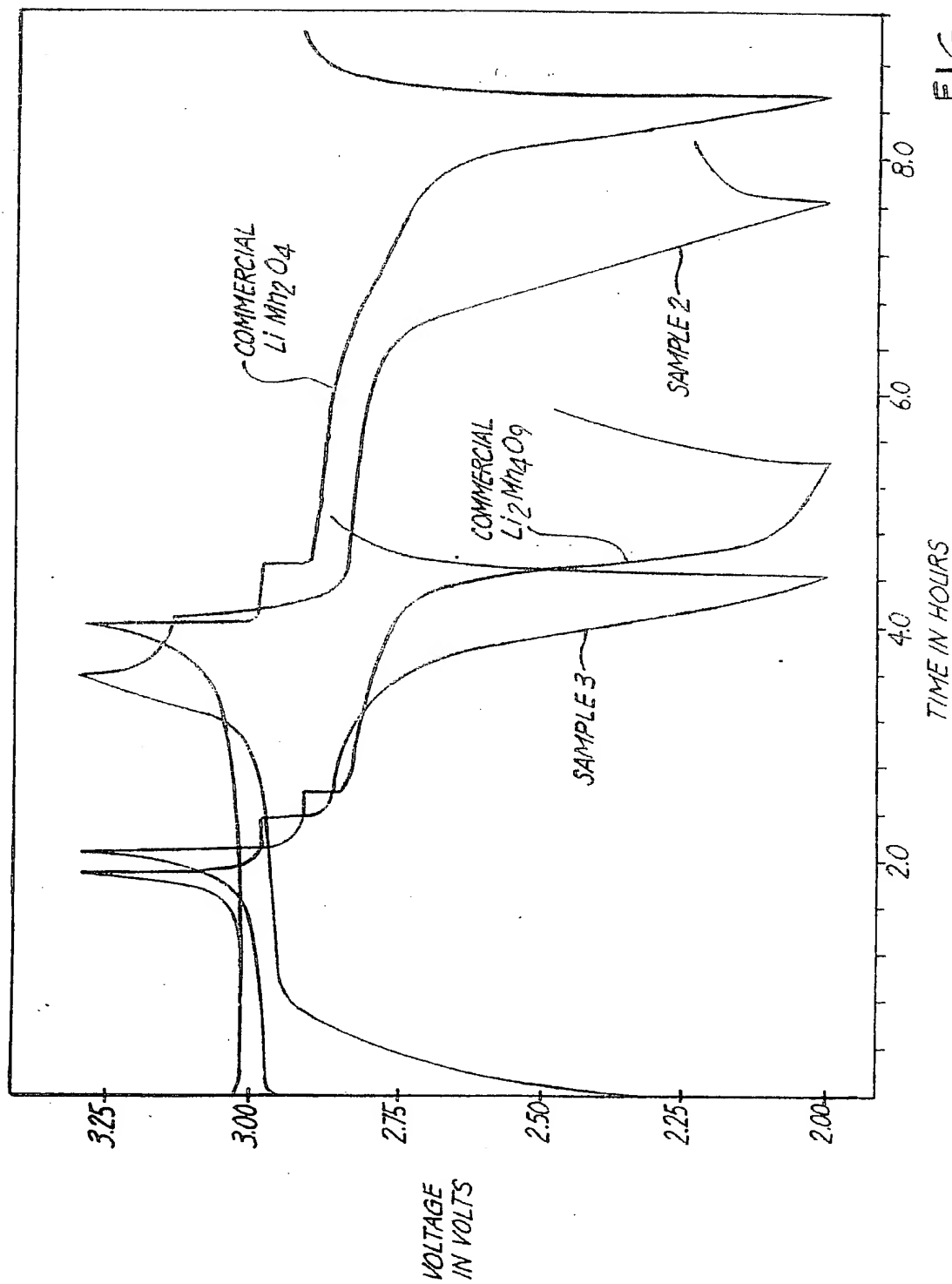


FIG. 49



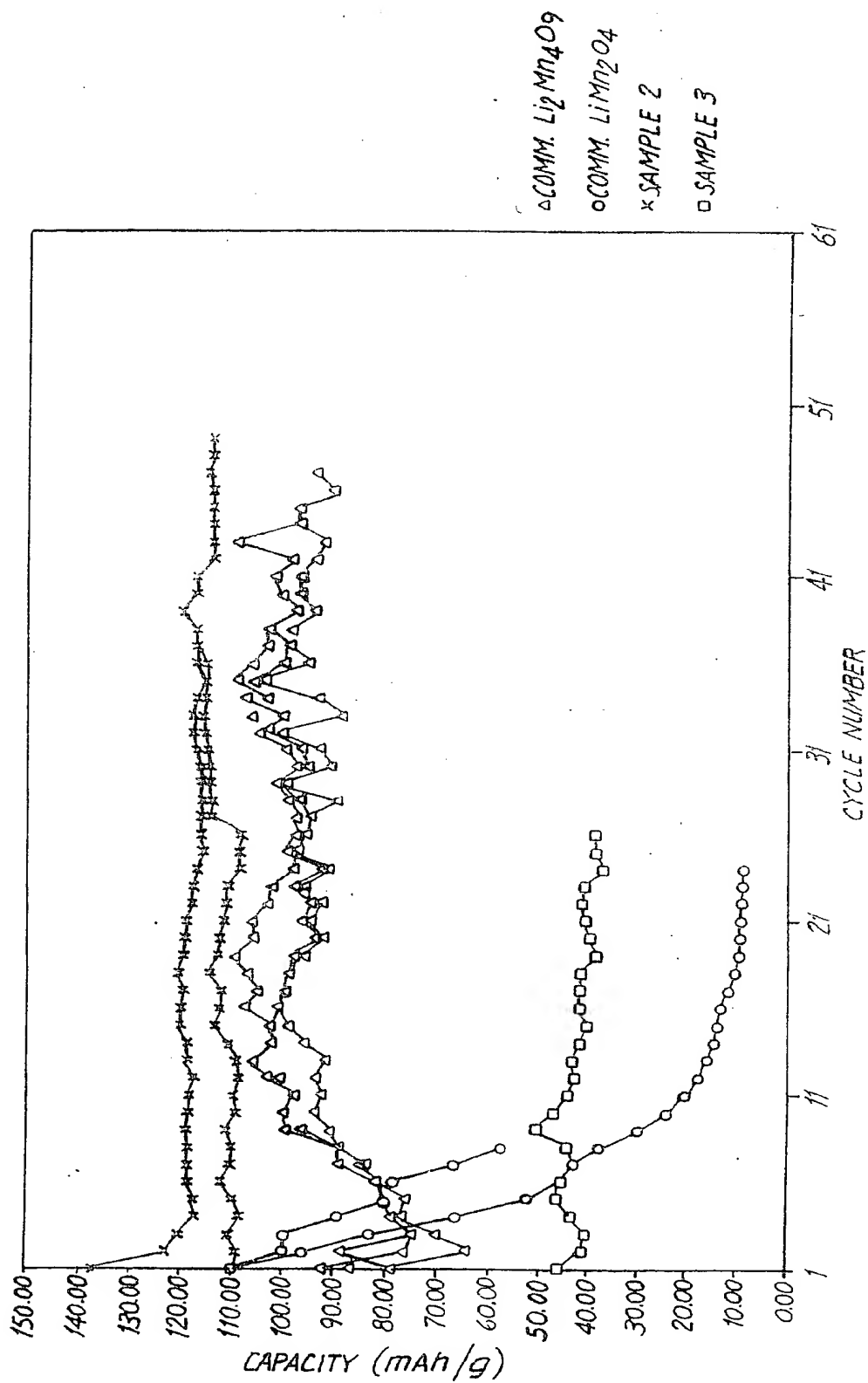


FIG. 50

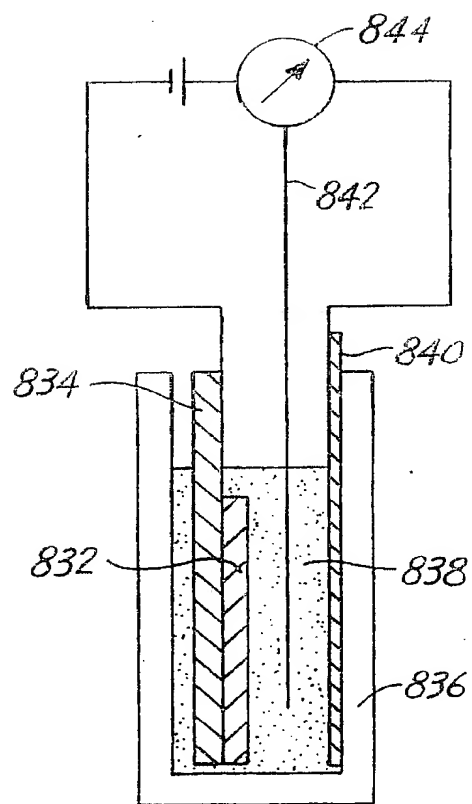
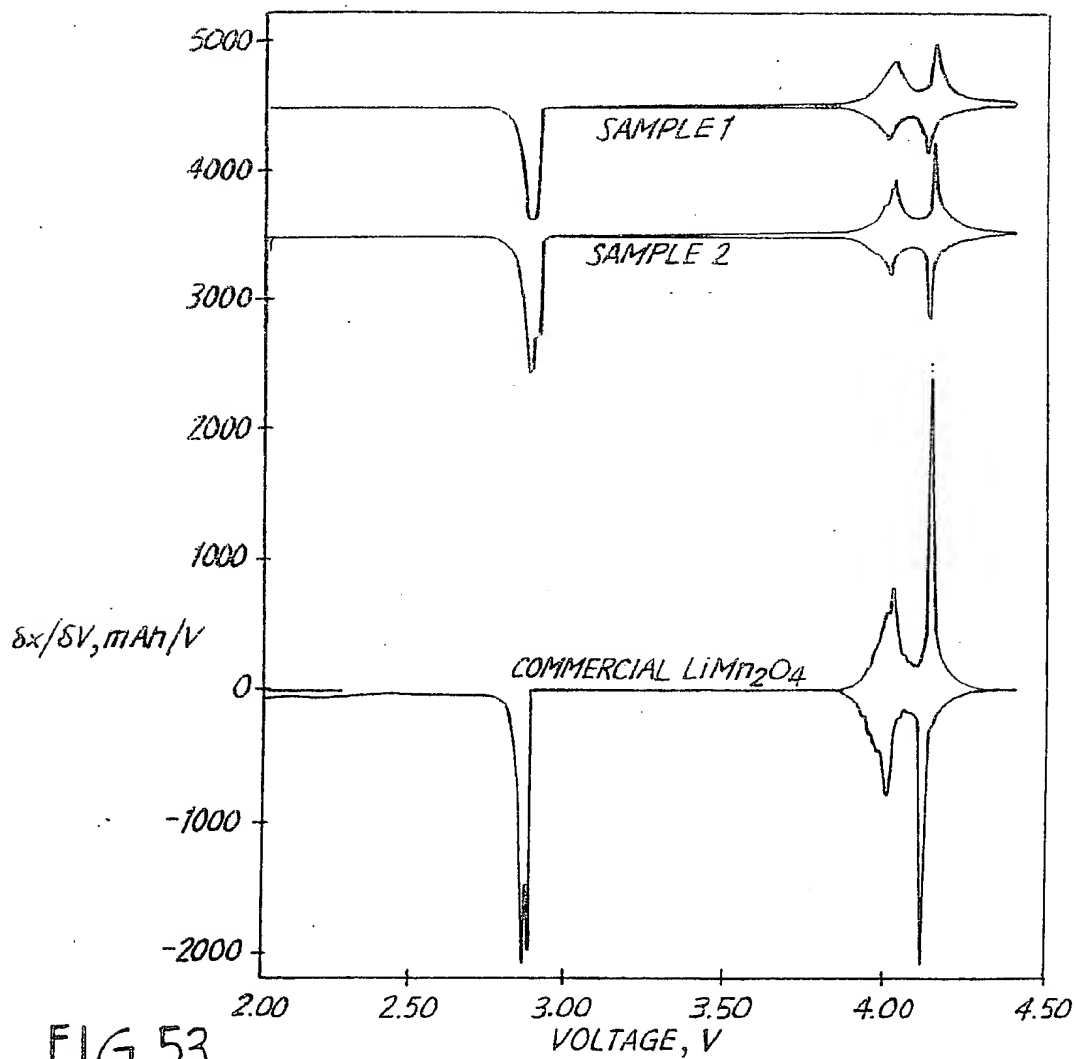
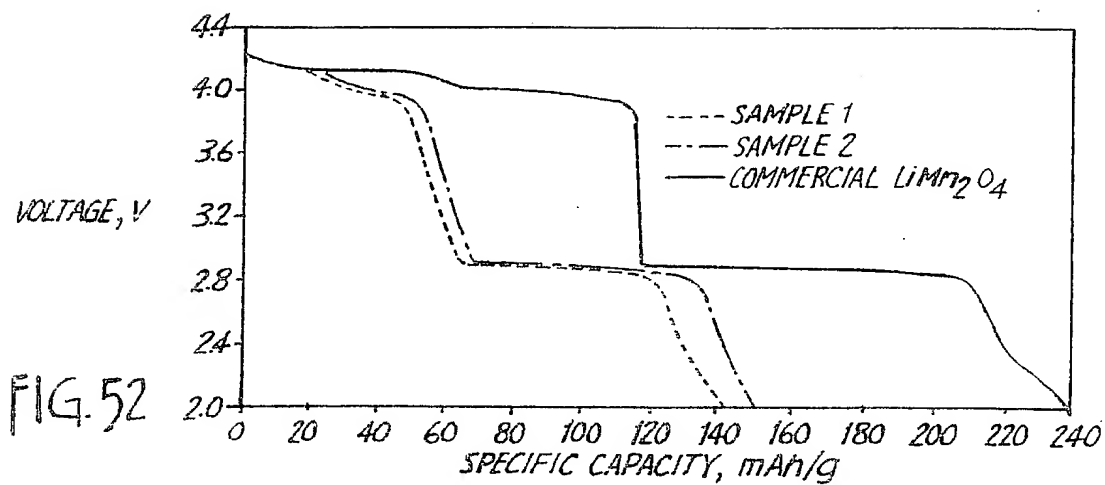


FIG. 51



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US99/26343

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : Please See Extra Sheet.

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/599, 605; 429/224; 502/324; 204/157.41, 157.42; 392/407, 416; 219/553.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,883,032 A (BOGDAN et al) 16 March 1999, col. 11, lines 55-68, col. 12, lines 7-18.	1, 5, & 6
Y	US 5,478,672 A (MITATE) 26 December 1995, abstract, col. 4, lines 10-29.	6, 7, & 25
Y	US 5,604,057 A (NAZRI) 18 February, 1997, abstract, col. 2, lines 10-11, lines 30-41, col. 3, lines 48-61, col. 4, lines 1-8 & lines 24, col. 5, lines 34-58.	8-9, 11-12, 18-19, 24, & 48-52
X/Y	US 5,807,646 A (IWATA et al) 15 September 1998, abstract, col. 3, lines 55-63, col. 4, lines 40-68, col. 5, lines 1-2, col. 7, lines 15-47.	1-5, 20, 40-44/45-47 & 71-75
Y	US 5,958,361 A (LAINE et al) 28 September 1999, abstract, col. 1-2, claims.	10, 14-17, 21, & 26

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	Y* document of particular relevance; the claimed invention can... be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

24 JANUARY 2000

Date of mailing of the international search report

10 FEB 2000

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Authorized officer

CAM NGUYEN

Telephone No. (703) 308-0661

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US99/26343

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,013,706 A (SCHRAMM et al) 07 May 1991, abstract, col. 2, claims.	13, 27-28, & 30-32
Y	US 5,874,058 A (SHEARGOLD et al) 23 February 1999, abstract, col. 4, lines 9-11, col. 5, lines 25-46.	37-38 & 40-44
Y	US 4,980,251 A (THACKERAY et al) 25 December 1990, abstract, col. 1, lines 6-43, claims.	35-47
X	US 5,965,293 A (IDOTA et al) 12 October 1999, col. 11, line 50, col. 12, lines 46-48.	53-55
Y	US 5,770,018 A (SAIDI) 23 June 1998, abstract, col. 2, lines 9-47, col. 10, lines 47-53, claims.	56-70

INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US99/26343

A. CLASSIFICATION OF SUBJECT MATTER:  
IPC (6):

C01G 45/12, 45/02; H01M 4/50; B01J 23/32; A45D 20/40; A21B 2/00; H05B 3/10.

A. CLASSIFICATION OF SUBJECT MATTER:  
US CL :

423/599, 605; 429/224; 502/324; 204/157.41, 157.42; 392/407, 416 :9/553.